

Review Article

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Heterogeneous catalysis: an alternative approach for energy and environment

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Abstract: The uncontrolled increase in population and human activities has led to a significant rise in the demand for energy resources. The excessive use of limited fuel sources, unplanned deforestation, and greenhouse gas emissions have necessitated the search for and development of alternative, sustainable energy resources that cause minimal or no harm to the environment. The introduction of green and eco-friendly technologies offers a potential solution to address the growing demand in fields such as petroleum and hydrogen production, with the ultimate goal of promoting environmental sustainability. This review article highlights recent innovations in the field of heterogeneous catalysis, focusing on the development of various catalytic materials and processes, as well as their future prospects for both industrial and academic advancements. A brief discussion is presented on the efficient performance of solid acid and base catalysts, metal-organic frameworks (MOFs), electrocatalysts, and photocatalysts. The discussed catalytic systems have been explored for their potential applications, including biodiesel and hydrogen production as alternative energy sources, as well as CO₂ reduction and the degradation of toxic dyes and organic pollutants for environmental remediation. Overall, the significance of heterogeneous catalysts has been explored, emphasizing their critical role in driving industrial progress and economic growth.

Keywords: heterogeneous catalysis; solid acid catalyst; solid base catalyst; photocatalysis; environmental remediation

1 Introduction

Catalysis is a fundamental element of many chemical processes and hence it is a main strength of all chemical

industries.¹ It is proven and now a day there is a growing concern about the catalysts that are environmentally friendly and safer technologies for the better industrial productions. Not less than 15 Nobel prizes have been awarded for studies on catalysis and many chemists around the world are repeatedly advancing the catalysts they have, and are motivated to discover new ones.

All the catalytic process can be applied either homogeneous or heterogeneous catalysis. Heterogeneous catalysis is a process in which catalyst being used is in a different phase than the reactants, i.e. the catalysis is usually in a solid phase and the reactant is in a liquid or in gaseous phase. As a part of catalysis, heterogeneous catalysis has prior importance in many areas of the chemical research for energy and environmental applications.^{2,3} Although, there are many advantages of homogeneous catalysis which is pH dependent and can function with wide pH range.³ Further, overall, most of (>80 %) chemical and bio-catalytic processes well established with heterogeneous catalysis and thus it is much successive catalytic process of vibrant branch of chemistry as well as pharmaceutical world. Figures 1–3 emphasizing the importance of the catalytic process and among all the process, how heterogeneous catalysis being a large part of chemistry itself can be found here.^{4,5}

The beginning era of heterogeneous catalysis, academic research and industrial processes were focusing on production of bulk chemicals and refining the oil as fuel on large scale requirement and it has been expanded rapidly in the recent decades.^{6,7} Heterogeneous Catalysis is now become a key factor for many industries for the conversion of petroleum and natural gas into cleaner and efficient fuels, but now there is a demand for the production of alternative fuels such as hydrogen and biofuels.^{6–8} Heterogeneous catalysis is still in use for the selective synthesis of special intermediates or products and fine chemicals in bulk production. Now a day it is possible to find the alternative route for the energy and environmental issues due to major advances in the design and development of catalyst at the molecular level.

In continuation, there are many efforts in progress to unlock energy sources that are much more difficult to use than fossil fuels, but are “greener”, where heterogeneous

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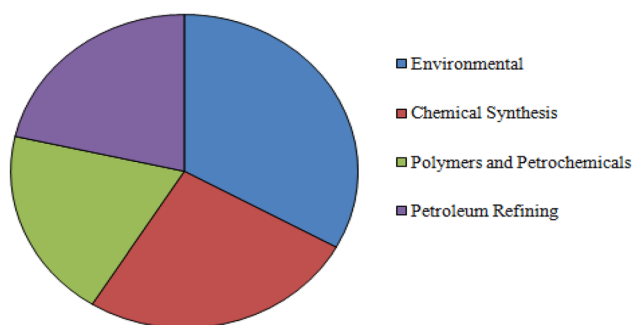


Figure 1: Global catalyst market share 2018 (%) by applications ⁴

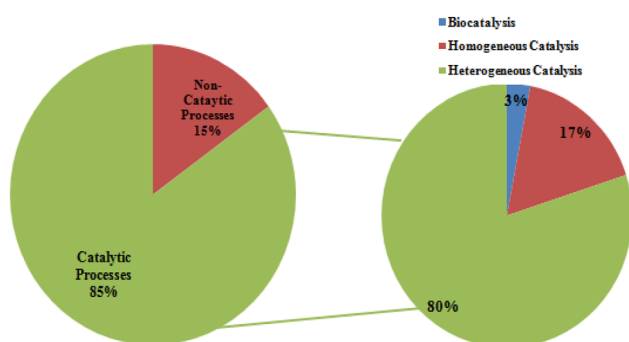


Figure 2: Involvement of catalytic and non-catalytic process to the chemical industries ⁵

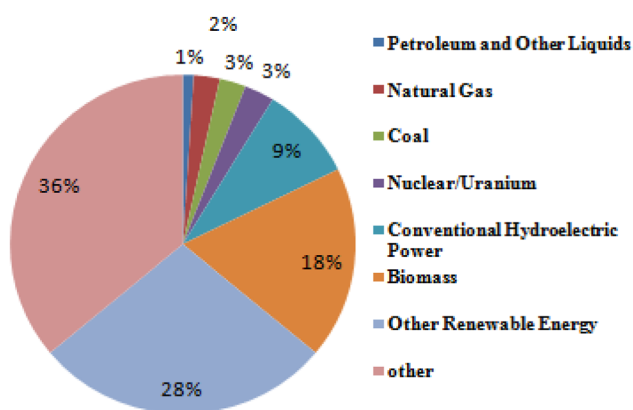


Figure 3: Involvement of heterogeneous catalytic systems to various fields ⁵

photocatalysis could make it economically feasible to produce hydrogen fuel from water splitting and leads to find novel methods to produce efficient energy sources from the raw resources such as CO₂,⁸ biomass⁹ etc. Green technologies have included heterogeneous catalysis as being advantageous for regeneration and reusability, production of no waste or very less amount of waste, easy set up process with lower cost, high thermal and chemical stabilities and

good selectivity of final product. Indeed, heterogeneous catalysis is being used for the environmental remediation for water, air and soil by applying an environmentally benign approach.

The conceptual platform for the practicable uses of catalytic systems can be defined by energy and mass dimensions. It consists of processes and materials being used with mass inputs in terms of raw materials to be converted into added-value ones directly or indirectly equal to the energy resources with or without emissions to be treated.^{10,11} In this context, the consumed energy can be considered an input for endothermic reactions, while the energy generated serves as an output for exothermic reactions. Light, heat and electrons are often considered specific resources that promote catalytic systems by adding energy, leading to processes such as photocatalysis or photoelectrocatalysis.^{10,12,13}

The types of catalytic systems can be identified based on the structure and nature of the catalytic materials, which impart their catalytic functionality. Table 1,^{14–31} and Figure 4 illustrate the most commonly used catalytic processes and materials.

There are also some drawbacks of heterogeneous catalysis such as it requires higher temperature and pressure for the reaction to occur, thus it requires higher energy consumption and therefore utility and energy related costs are very high.² To develop and design a highly efficient and environmentally-friendly catalytic materials and

Table 1: Types of catalytic processes commonly used.

No.	Catalytic processes	Ref.
A Oxidation		
1	Advanced oxidation process	14–17
	– To eliminate the degradability of organic pollutants like dyes	
	– Decomposition of water into hydrogen and oxygen	
	– Oxygen evolution reactions (OERs)	
2	Oxidation of SO _x , NO _x and CO _x	18
	Oxidation of carbon monoxide to carbon dioxide (CO ₂)	19
3	Oxidation of alkanes, alkenes and aromatics	20
4	Oxidation of alcohol (methanol to CO ₂)	21
B Hydrogenation		
5	Hydrogenation process of vegetable oils	22
6	Hydrogenation of alkenes and aromatics	23
7	Formation of ammonia	24
8	Hydrogenation process of CO ₂	25
9	Hydrogenation or hydrocracking of plastic and rubber waste	26
C Dehydrogenation		
10	Dehydrogenation for H ₂ production	27
D Reforming		
11	Catalytic dry reforming of methane	28
12	Catalytic reforming of biofuels	29
13	Catalytic reforming of oxygenates	30
14	Dry reforming processes for hydrogen production	31

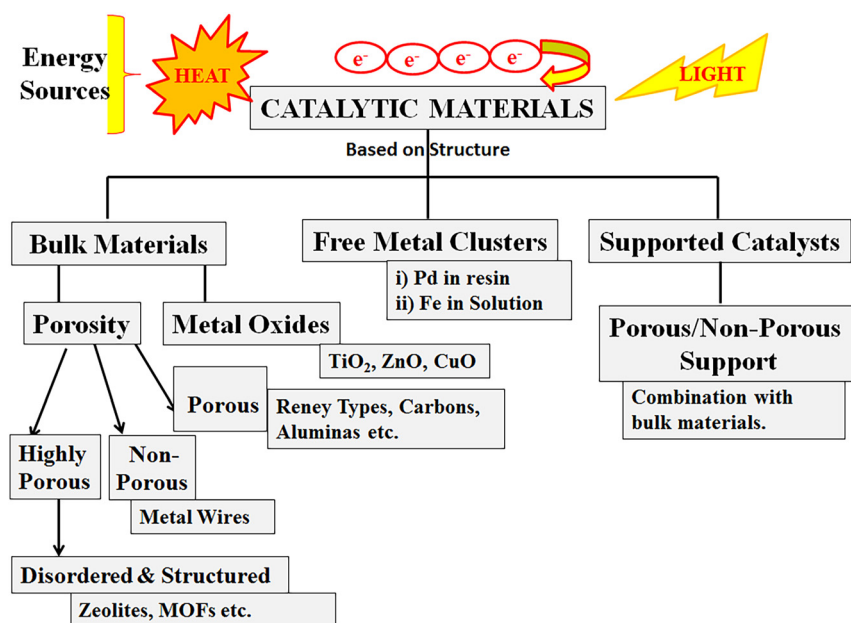


Figure 4: The types of catalytic systems based on structure.

systems are very effective approaches to generate novel energy sources and remediation of contaminated soil, air and wastewater.^{6,7b} Thus, the bridging connection between a material structure and chemistry with efficient performance of heterogeneous catalyst would provide rational informations for catalyst design and addressing the challenges in promising use in the research area of energy resources.

The current review article shows recent development and progress in heterogeneous catalysis for energy and environmental applications. Heterogeneous catalysis consists of many subclasses depending on nature and structure of the catalyst used in solid phase such as solid acid catalyst, solid base catalyst and nano catalyst.

2 Energy applications

2.1 Biodiesel production

Currently, the use and storage of fuel energy for economic development and finding of an alternative fuel sources are in prior demand due to the ever-increasing world population. It is now an urgent worldwide issue to implement the possible all the efforts for the sustainable automotive fuels.⁷ Since, last few decades, the biodiesel production has been promoted on the large scale as a safe and novel technology. Biodiesel belongs to the class of renewable and sustainable fuel source receiving more attention as rapidly growing field with high potential rather than other energy sources and evidently beneficial for a long-term investment.^{32–34}

Processes for biodiesel production can be classified as catalytically, chemically (base or acid catalysis), biologically (enzyme catalysis) and non-catalytic processes. Chemically, biodiesel (alkyl-ester derivatives) is usually produced by chemical catalytic transesterification of refined vegetable oils/waste cooking oils (long chain fatty acids) or animal fats. The chemical catalysts used earlier are strong acidic (HCl, H₂SO₄, HF, *p*-toluenesulfonic acid) or basic solutions (NaOH, CH₃ONa and KOH).^{7b}

Now days, a “green” approach for biodiesel production has been adopted the use of sustainable solid acid catalysts as replacements for such liquid acid catalysts so that the use of harmful/corrosive substances and unwanted formation of toxic wastes could be avoided. With remarkable developments and fruitful researches reported in the past few years for the industrial production, heterogeneous catalysis is growing up in the market for the biodiesel production.^{7b,33a} Heterogeneous catalytic transesterification is a process where the catalysts remain in different phase to that of the reactants and provides easier separation of biodiesel from glycerol.^{35–37} The catalytic conversion of oil into biodiesel is slowly but the resulting biodiesel could be possible in an economical way.^{38,39} Firstly, surface morphology characteristics, having large pore size to minimize diffusion problems is an ideal characteristic of a solid catalyst as being a part of heterogeneous catalysis. Another one, is deactivation, mainly achieved because of availability more active catalytic sites, high catalytic stability versus leaching and the probability to tune the hydrophobicity of the surface with the repulsion of highly polar compounds.⁴⁰ From the literature, solid base catalysts such as base zeolites,

alkali earth metal oxides, hydrotalcites (or layered double hydroxides), alumina loaded with various compounds and mixed oxide have been quite successful with high conversion and yield of biodiesel obtained.^{33b}

2.1.1 Solid acid catalyst (SAC)

SAC can be defined on the basis of nature and number of present active acid sites (Brønsted or Lewis acidity), availability of the acid sites and morphology of the support. Therefore, the acid catalysts could be used directly for biodiesel formation from low-grade, highly-acidic and water-containing oils. Thus, solid acid catalysis is now well established as benign alternatives to the unrecyclable-homogeneous acid catalysts and succeeds in the petrochemical industries. Many more benefits avail to this class of catalysts such as, (i) the catalysts could be modified and tunable, selective and easy regenerate and reuse, (ii) minimize product contamination through easy separation from target product, (iii) elimination of washing step particular for biodiesel production, (iv) replaced use of corrosive liquid acids and thus corrosion issue could be minimized, (v) could be employed in continuous flow process, (vi) minimum catalyst deactivation, (vii) catalyst could be rapidly prepared through economically and environmentally affordable process.³ The surface morphology of the solid catalyst plays a key role for better catalytic performance through selective adsorption of reactant molecules and converts into the desired product. However, many more finding has to search out to connect and fill the knowledge gap between the fundamental concept of reaction pathway and the mechanisms of reactants on the solid catalysts.

They are mainly used for important acid catalyzed organic transformations such as Friedel-Craft alkylation/acylation, esterification/transesterification, acetal/ketal formation etc.^{7b} Literature report highlighting the extensive use of solid acid catalysts for biodiesel production through esterification or transesterification processes. For example, the mechanism of the acid catalyzed transesterification reaction of triglycerides is well understood.^{6,41,42} Still there are some challenges facing for biodiesel production such as to increase rate of reaction and to reduce unwanted side reaction. Thus, these challenges lead to develop a novel, efficient and stable catalytic system and more efforts for reduction in cost of preparation the catalyst and sequentially reduced biodiesel production costs. There is lots of research work in progress to overcome the said challenges through potential application of various solid acid catalysts for biodiesel production.

The ideal characteristics of a solid acid catalyst are strong Brønsted and/or Lewis acid properties, unique porosity or textural properties and a hydrophobic surface. Till date, the catalytic potential of solid acids have been reported for the biodiesel production such as acidic inorganic ion exchangers, acidic clays, metal oxides, mixed metal oxides, H-form zeolites, heteropolyacids (HPAs), modified silica, acidic ionic liquids, hybrid organo-inorganic materials and carbon based materials.

The Brønsted acid sites are highly polarized hydroxyl groups at the surface of the catalyst that serve as the H⁺-donor, while the Lewis acid sites are coordinatively unsaturated cationic sites, which leave the exposed M⁺ ion to interact with guest molecules and act as the acceptor of the electron-pair. With respect to base catalysts, biodiesel production processes based on the use of solid acid catalysts are effective alternatives to the conventional processes because of their easy workup and the simultaneous promotion of esterification and transesterification reactions without soap formation.

Zeolites and zeolite type materials: Zeolites are naturally abundant three dimensional frameworks with crystalline structures of aluminosilicates interlinked by oxygen atoms. They contain Al, Si and O in their framework, and cations, water and/or other molecules within their pores.³⁴ They are well established and robust materials because of having molecular porous structure with channel of uniform sizes gives materials to be ion exchange characteristic. The catalytic activity depends on replacement of Si⁴⁺ by Al³⁺ with crystalline SiO₂ framework which generates negative charges in the catalyst framework and thus improves catalytic activity. Interestingly, the adsorption ability could be modified through synthesis methods as expected due to the strong electric field created by the loosely held cations within the catalyst framework. Thus, desired catalytic performance in term of good activity and selectivity could be obtained as it has ability to introduce active sites within the pores and channels.³

Zeolite can accommodate number of cations such as Na⁺, K⁺, Ca²⁺, Mg²⁺ and many more from which it has its basic nature. H-ZSM-5, H-MOR, H-BETA and H-USY are H⁺ ion exchanged acid form zeolites found to be not much catalytic active for esterification or transesterification reactions of biodiesel production due to internal diffusion limitations of the bulky reactant molecules into the micro-pores of zeolites.³ Zeolites Y are weak solid acid catalyst while Zeolites β are three-dimensional structure of 12-membered ring channels with high silica content having both Lewis and Brønsted-acid sites. Lewis-acid sites are mainly present in the micro-porous walls. Zeolite β does not exhibit high activity in transesterification, but it could be used for

selective removal of FFAs in waste oil. Silicoaluminophosphates, the recently developed Zeolite types materials for examples, SAPO₄, ALPO₄, MeAPSO₄ and MeAPO₄ could be synthesized with coordinated Al, Si, P, transition metals and other elements.³

The catalytic activity of the protonated form of H-Y zeolite (Faujasite with high Si/Al ratio) has been investigated as solid acid catalyst for esterification of oleic acid with methanol.⁴³ At optimized conditions, methyl esters production yield reaches up to ~95 % and the used catalyst could be regenerated easily and reused for the same. Septiani et al.⁴⁴ have prepared Zeolite ZSM-5 and studied its catalytic activity for the transesterification of vegetable oil for biodiesel production. The results of the catalytic reaction show a maximum biodiesel yield of ~92 % at the optimized reaction time and temperature. Zeolite and zeolite-based heterogeneous catalysts^{43–69} for biodiesel production have been summarized in Table 2.

Metal oxides: Metal oxides are materials of typical characteristics such as thermal and mechanical stability, high specific surface area, and large pore size and pore volume. Thus, they are extensively being used as catalyst supports for catalytic purpose.

Table 2: Zeolites and zeolite-based heterogeneous catalysts for biodiesel production using esterification or transesterification reactions.

Sr. No.	Catalysts	Esterification/trans-esterification reactions molar ratio of oil: alcohol	Ref.
1	H-Y(80) zeolite (faujasite with high Si/Al ratio)	Esterification of soybean oil Oil: methanol = 1:3, 1:6 and 1:9	⁴³
2	Zeolite ZSM-5 prepared from rice husk ash	Transesterification of vegetable oil Oil: methanol = 1:3	⁴⁴
3	H-zeolite	Transesterification of vegetable oil Oil: methanol = 19.4:1	⁴⁵
4	Y-type zeolites with Al ₂ O ₃ and Na ₂ O	Transesterification sunflower and waste oil Oil: methanol = 12:1 to 48:1	⁴⁶
5	Faujasite (FAU)-type zeolite prepared using Irish shale rock	Esterification of vegetable oil Oleic acid: ethanol = 4:1–15:1 by mass	⁴⁷
6	KOH/zeolite prepared by impregnation in KOH	Transesterification of waste sunflower oil Oil: methanol = 1:1.51	⁴⁸
7	KOH/Bentonite prepared by impregnation method	Transesterification of refined soybean oil Oil: methanol = 6:1 –14:1	⁴⁹
8	Y-type zeolites, with different Al ₂ O ₃ and Na ₂ O percentage	Transesterification of vegetable oil Oleic acid: methanol = 6:1	⁵⁰

Table 2: (continued)

Sr. No.	Catalysts	Esterification/trans-esterification reactions molar ratio of oil: alcohol	Ref.
9	ZSM-5 and beta hierarchical zeolites	Transesterification of algae oil Oil: methanol = 100:1	⁵¹
10	Alkali loaded low-Al zeolite beta	Transesterification of triolein Oil: methanol = 1:15 (w/w)	⁵²
11	Zeolite linde type a (LTA, dehydrate form)	Transesterification of triolein (methanol in excess)	⁵³
12	KOH/Zeolite prepared by impregnation method	Transesterification of triglyceride with excess methanol	⁵⁴
13	Natural zeolite bayah banten with KOH impregnation method	Transesterification using vegetable oil <i>Jatropha</i> oil: methanol = 1:1	⁵⁵
14	Zeolite based catalysts prepared from fine powder and kaolinite using pelletization method	Simultaneous trans-esterification and esterification of waste cooking oil Oil: methanol = 1:5	⁵⁶
15	Natural zeolite with potassium impregnation	Transesterification of rice bran oil Oil: methanol = 1:6 to 1:12	⁵⁷
16	Zirconia supported on Indonesia natural zeolite	Esterification of palm oil sludge Oil: methanol = 1:4	⁵⁸
17	KOH/NaY zeolite prepared by the impregnation method	Transesterification of palm oil Oil: methanol = 1:15	⁵⁹
18	KOH/Al ₂ O ₃ with varying KOH loadings prepared by the impregnation of the Al ₂ O ₃ support	Transesterification of vegetable oil Oleic acid: methanol = 1:15	⁶⁰
19	NaX zeolite impregnated with mixture of CaO nanoparticles/ethanol	Transesterification sunflower Oil: methanol = 1:6	⁶¹
20	Sodic potassic clinoptilolite and sodic potassic calcic clinoptilolite zeolites	Transesterification of waste cooking oil Oil: methanol = 68–27 (vol%)	⁶²
21	Lanthanum-natural zeolite (La/Zeolite)	Transesterification crude palm oil Oil: methanol = 1:9	⁶³
22	ZnO/Zeolite, PbO/Zeolite	Esterification of <i>Jatropha</i> oil Oil: methanol = 1:6	⁶⁴
23	Zeolite X and a from flyash using hydrothermal treatment	Transesterification of refined mustard oil Oil: methanol = 1:6	⁶⁵
24	Zeolite MCM-22 and zeolite beta	Transesterification of triolein in excess methanol	⁶⁶
25	Zeolites loaded with CH ₃ COOK	Transesterification of <i>Jatropha curcas</i> Oil: methanol = 1:10	⁶⁷
26	HZSM-5 and HZSM-5 impregnated with sulfated lanthanum oxide (SO ₄ ²⁻ /La ₂ O ₃)	Esterification of oleic acid Acid: methanol = 1:5, 1:10 and 1:20	⁶⁸
27	Commercial H-Y and ZSM-5 zeolite	Esterification of palmitic acid Acid: methanol = 1:2	⁶⁹

The typical superacids such as $\text{SO}_4^{2-}/\text{ZrO}_2$, $\text{SO}_4^{2-}/\text{TiO}_2$, $\text{SO}_4^{2-}/\text{Ta}_2\text{O}_5$, $\text{SO}_4^{2-}/\text{Nb}_2\text{O}_5$ etc.^{7b} They possess potential economic and green benefits for a number of hydrocarbon reactions under mild reaction condition and thus, interest has been generated to use of such materials for transesterification and esterification reactions to produce biodiesel.⁷⁰ Herein, an interesting factor about the metal oxides (ZrO_2 , TiO_2 , Ta_2O_5 , Nb_2O_5), they possess the both Brønsted and Lewis acidity that can be improved by modifying its surface by sulfate groups which makes materials to be promising catalyst to promote protonation in the esterification process.⁷¹ Castro et al.⁷² have studied heterogeneous solid acid catalysis for esterification and transesterification processes for biodiesel production as renewable fuels to meet the future societal requirements. The authors have prepared sulfated niobium oxide ($\text{Nb}_2\text{O}_5/\text{SO}_4$) impregnation method and used as solid acid catalyst for biodiesel production from macaw palm oil via high free fatty acid content transesterification with ethanol. As results, the catalyst $\text{Nb}_2\text{O}_5/\text{SO}_4$, exhibits excellent catalytic activity towards biodiesel production (about ~99 % ester content). The spent catalyst could be reused up to five consecutive catalytic cycles which shows excellent yield of the desired products and the reducing of the yield after fifth catalytic cycle could be due to the handling/physical loss of the catalyst during recycles and regeneration.⁷² Sulfated zinc oxides $\text{SO}_4^{2-}\text{-ZnO}$ and $\text{SO}_4^{2-}/\text{ZnO}$ have been synthesized by co-precipitation and impregnation respectively and characterized as active solid acid catalyst.⁷³ The prepared catalysts have been used for trans-esterification of soybean oil with methanol to compare their performance for biodiesel production. As results at optimized reaction conditions, $\text{SO}_4^{2-}\text{-ZnO}$ prepared by co-precipitation method exhibit highest catalytic activity and obtained FAME yields of ~80 %.

Sulfonic ion exchange resins such as Amberlyst-15, -16, -35, -36 and -131,^{74,75} Nafion resins^{76–80} as SAC-13 and NR50 and EBD-100, -200 and -300,⁸¹ were commonly used heterogeneous catalysts and found to be effective in liquid phase esterification and trans-esterification reactions. The protons bonded to the sulfonic groups are the responsible for the strong acidic active sites which are available on the cross-linked polymeric matrix of these ion exchange resins. The catalytic activity more depend on their surface properties which in turn effective populations of the acidic active sites for the trans-esterification and esterification reactions.

Mesoporous silica (SBA-15) supported $\text{ZnO}/\text{SBA-15}$ and $\text{MgO}/\text{SBA-15}$ have been prepared and characterized for solid acid catalytic activity. The results show that catalysts exhibit good catalytic activity and promote the esterification of

lauric acid with 1-butanol to produce biodiesel (~81 % yield of butyl ester) under atmospheric pressure and reflux conditions.⁸² Tesser et al. have prepared Niobia supported catalyst by impregnation of silica pallets with loading of Nb and characterized for catalytic characteristics. The prepared solid acid catalyst has been used in both transesterification (free acid methyl ester conversion) and esterification (free fatty acid conversion) reactions of triglycerides for biodiesel production. The study, Nb supported on silica found to be much active in both the mentioned reactions with no loss of catalytic activity in the continuous run of 100 h but slow leaching of Nb observed which could be reduced the catalytic potential.⁸³ Xie et al. prepared lithium doped zinc oxide (Li/ZnO) using impregnation method followed by calcination at different temperatures and evaluated its catalytic activity for transesterification of soybean oil with methanol at optimized reaction conditions.⁸⁴ As results, Li/ZnO exhibits good catalytic activities towards soybean conversion to ester as obtained ~96 % yields. The catalytic sites are in basic nature which is due to formation of Li_2O from thermal decomposition of LiNO_3 at higher calcination temperatures. The authors also have prepared $\text{CaO-MoO}_3\text{-SBA-15}$ by incipient impregnation method with different calcination temperatures and tested for the similar transesterification reaction of soybean oil with methanol for biodiesel production.⁸⁵ The prepared solid catalysts, a catalyst with loading of 40 % and calcined at 550 °C shows highest catalytic activity (~83 % yield of oil conversion) at the optimized the reaction conditions. The catalyst could be easily reversed and reused without loss of its potential catalytic activity.⁸⁵ Viswanathan et al.⁸⁶ prepared sulfated $\text{Fe}_2\text{O}_3\text{-TiO}_2$ from ilmenite and calcined for different temperatures. The prepared catalyst examined for its acidic active sites and used for conversion of vegetable oil to biodiesel via transesterification reaction with methanol. As results, the catalyst calcined below 500 °C shows higher conversion of vegetable oil with remarkable yield of biodiesel which is attributed to the high affinity of hydroxyl groups of methanol on $\text{Fe}_2\text{O}_3\text{-TiO}_2$. The removal of sulfate groups has been observed during calcination on above 500 °C could reduce % yield of biodiesel production.⁸⁶

Mixture of strontium and nickel oxide has been synthesized by coprecipitation method followed by different calcination temperatures and characterized for catalyst properties.⁸⁷ The prepared catalysts have been used as heterogeneous catalysts for the transesterification of macaw palm oil with methanol for biodiesel production. The catalyst with the calcination temperature of 1,100 °C has highest catalytic activity as achieved ~97 % conversion at the optimized reaction conditions as well as recycling studies also favoring the good % yield for the five catalytic runs.⁸⁷

Ong et al.⁸⁸ have studied catalytic activity of the carbon supported CuO catalyst in which the copper nanoparticles have been synthesized by sol-gel method and the nanoparticles impregnated into the pore network of the carbon supported. The prepared catalysts used in esterification of free fatty acid in the rubber seed oil and ~95 % of the free fatty acid conversion was obtained at the optimized reaction conditions. The catalytic performance is comparable to the liquid acid H_2SO_4 as well as compared with other heterogeneous catalysts, the carbon supported-CuO could performed at lower temperature. The reusability study also shows about easy recovery and separation of the catalyst after process completion however it found with lower activity in the use of first catalytic cycle. Zhang et al.⁸⁹ have prepared sulfonic/carboxylic dual-acid catalyst based on sulfur-rich graphene oxide (GO-S) as cost effective SAC used for the esterification of the oleic acid with methanol to produce methyl-ester as biodiesel. The results show, GO-S exhibits good catalytic performance in term of activity and reusability which has high TON factor compared to other carbon based SACs. Having a two-dimensional layered structure and the strong synergetic effect between $-\text{SO}_3\text{H}$ and $-\text{COOH}$ groups on the graphene nano-sheets, are the key factors for the catalytic activity of GO-S.⁸⁹ The study reveals the promising use of the GO-S in the esterification of the waste fatty acids to convert into the valuable biofuels.

2.1.2 Solid base catalysts

Metal oxides: Recently, alumina has been exhibited as a good support for catalytic material in catalytic process due to having good characteristics such as thermal and mechanical stabilities, high surface area, large pore size and pore volume.⁹⁰ Anisuzaman et al. have prepared CaO-supported basic alumina catalyst by impregnation method followed by calcination temperatures and characterized for their catalytic properties.⁹⁰

Alkali metal oxides (CaO, MgO and BaO) doped silica (SiO_2) has been synthesized using sol-gel method followed by different calcination temperatures and used as base catalysts for the biodiesel production.⁹¹ The catalytic transesterification reaction of corn oil with methanol shows that the catalyst CaO/ SiO_2 exhibits highest biodiesel production compared to other catalysts with the purity and yield of ~97 % and ~82 % respectively.⁹¹ Ismail et al. have synthesized calcium oxide (CaO) from mud clam shell and used as potential heterogeneous catalyst for the biodiesel production.⁹² The results of the catalytic transesterification reaction of castor oil with methanol show a good efficiency of CaO catalyst with the obtained ~96 % yield of biodiesel formation using the optimum reaction conditions as well as

the CaO catalyst from mud clam shell could be recycled and reused up to five catalytic runs.⁹² Thitsartarn et al. also have reported calcium doped cerium-incorporated SBA-15 (Ca/CeS) synthesized by direct synthesis of Ca-incorporated-SBA-15 followed by impregnation of CaO.⁹³ The catalytic studies, the Ca/CeS shows excellent catalytic performance for biodiesel production through catalytic transesterification of palm oil with methanol and also the highest catalytic activity found amongst the other supported catalyst such as CaO/ CeO_2 and CaO/ CeO_2 -SBA-15. As being heterogeneous catalysis, negligible leaching of elements was observed due to strong interaction between CaO and CeS support. Furthermore, beneficially the catalyst could be reused for 15 catalytic runs with insignificant decrease in catalytic activity which reveals the very good efficiency of the catalyst for the biodiesel production.⁹³ Heterogeneous strontium oxide/calcium oxide (SrO -CaO) mixed metal oxides catalyst has been used in the ultrasonic-assisted transesterification of *Jatropha* oil into biodiesel. The catalyst characterization and the catalytic studies show that the prepared catalyst exhibits high efficiency for the conversion of *Jatropha* oil into biofuels.⁹⁴

Biodiesel production from non-edible *Jatropha* oil has been reported using acid-base bi-functionalized CaO- La_2O_3 heterogeneous catalyst.⁹⁵ The catalyst comprising CaO and La_2O_3 mixed metal oxides with different Ca/La ratios have been prepared by using co-precipitation method. As results, the highest biodiesel yield of ~98 % has been achieved and binary catalyst system found to be more stable which was supported by recycling and reusability of the catalyst even after four catalytic cycles. The observed very good catalytic activity in the mixed metal-metal oxide is due to well dispersion of CaO on composite surface which enhance both surface acidic and basic sites as compared to that of bulk CaO and La_2O_3 metal oxide.⁹⁵ Wang et al.⁹⁶ have reported a series of acid-base bi-functional metal-boron catalysts prepared by sol-gel method followed by calcination temperatures and characterized by spectral and surface characteristics. Amongst the prepared catalysts, the Ca-Boron (700 °C) catalyst shows highest catalytic performance for the production of biodiesel with high acid value (yield of ~98 %) through transesterification reaction of non-edible oil (*Jatropha*) with methanol using optimized reaction conditions. The catalyst exhibits a good stability and reusability which makes it promising acid-base bi-functional catalytic material for the biodiesel production.⁹⁶

Lee et al.⁹⁷ have studied the catalytic activity of mixed metal oxides (MMOs) (CaO-MgO, CaO-ZnO, CaO- La_2O_3 and MgO-ZnO) synthesized by co-precipitation method followed by calcination at different temperatures. MMOs contained high basicity and strong basic strength compared to single

metal oxide which shows excellent catalytic performance in the transesterification process. As results of the studied catalytic reactions, the Ca-based MMOs catalysts exhibit highest catalytic activity in term of ~90 % yields of biodiesel production and reusability with low metal leaching. Amongst three Ca-based MMOs, CaO–ZnO has comparative high conversion rate with ~94 % yield of biodiesel and could be used for four catalytic cycles with negligible loss of activity.⁹⁷ Yigezu et al.⁹⁸ have studied catalytic activity of metal oxides such as Co_3O_4 , KOH, MoO_3 , NiO, V_2O_5 and ZnO for catalytic conversion of oil into organic liquid products. As results, the catalysts are found to be suitable and active solid catalysts for the catalytic cracking of vegetable oil for bio-fuel production.⁹⁸

The review chapter more discussed on basic mixed-metal oxides (CaO and MgO based), acidic mixed-metal oxides (SiO_2 , SnO_2 and Fe_2O_3 based) and acid-base bi-functional mixed-metal oxide (ZnO – La_2O_3 , MnCeO_2 and SrO – ZrO_2).⁶⁰ Many of the catalysts studied are excellent in the catalytic performance for the biodiesel production through esterification or *in-situ* esterification and transesterification processes.⁶⁰ Refaat has briefly presented a review chapter on synthesis methods and characterization of various metal oxides commonly being used in the esterification and transesterification of oil with alcohol for the biodiesel production.⁹⁹ The chapter highlighting about the catalytic activity of alkali earth metal oxides, transition metal oxides, mixed metal oxides and supported metal oxides as heterogeneous catalysts in the transesterification reaction. The author has discussed about the catalyst selection and catalyst preparation for efficient transesterification process as well as explained the deactivation issue of the catalyst as important as catalyst activity. The author has concluded about the synergy between emerging technologies as ultra-sonication and microwave irradiation, on one side, and heterogeneous catalysis, on the other side, for the production of biodiesel appears to be very promising.⁹⁹ Cardoso et al.¹⁰⁰ have reported a review article about the importance characteristics related to the synthetic route, stability and activity of the tin catalysts in the esterification of triglycerides for biodiesel production with high free acid methyl ester content. They have explained the main structural features and physical properties of the solid tin catalysts such as SnO_2 , SO_4^{2-} – SnO_2 , SO_4^{2-} – SnO_2 – Al_2O_3 , SO_4^{2-} – SnO_2 – Fe_2O_3 with different Sn to Al and Fe molar ratio, for better understanding and significant contribution for the biodiesel production.¹⁰⁰

Vedrine has reported a review chapter on the fundamentals of heterogeneous catalysis and on metal oxides special members of heterogeneous catalyst family, acid-base catalyzed reactions, selective partial and total oxidation, de-pollution, biomass conversion and green

chemistry including photocatalysis.⁶¹ The main focus of the article is discussion on current industrial applications of supported and non-supported metal oxide catalysts. Chouhan et al. have presented a comprehensive review on a large number of modern heterogeneous catalysts for biodiesel production.⁶ The report content discussed on alkali metal oxides, alkaline metal oxides and their derivatives, transition metal oxides, mixed-metal oxides (MMOs), ion exchange resin type oxides, sulfated oxides as solid acid catalysts, carbon and boron group base solids and enzyme based solid catalysts. The authors have discussed on the catalytic activity, selectivity, catalyst loading, catalyst reusability and summary of the future scopes.⁶ Diamantopoulos et al. have introduced heterogeneous catalysts as important materials for the biodiesel production.¹⁰¹ The authors have discussed on zeolite, mixed oxides, sulfonic acid group catalysts, sulfonic acid modified SiO_2 , HPAs and polyoxonetalates, supported and substituted HPAs and solid acid catalyst based in waste carbon. They have explained the catalytic activity of these catalysts in terms of their efficiency and reusability. The review reveals the fact about the advantages of the solid acid catalysts although they are not much active than base catalysts, benefits such as procedure simplification and positive environmental impacts, support the utility of biodiesel production by using various efficient solid acid catalysts. The lower catalytic activity of the solid acids compared to other catalyst for transesterification reactions is usually compensated by operating at higher calcination temperatures (120–450 °C).¹⁰¹

Table 3 summarizing the metal oxides and mixed-metal oxides (MMOs)^{73–105} as heterogeneous catalysts for biodiesel production via esterification or/and transesterification reactions.

Hydrotalcites: The hydroxyl carbonates of magnesium and aluminum, hydrotalcites (HTs) are minerals belonging to the family of anionic clays, containing anionic species in the inter-lamellar space. HTs are being used as solid catalysts due to their physicochemical properties, such as thermal stability, porosity, specific large surface area (after calcination), memory effect, basicity or/and acidity, and anion exchange capacity.^{106,107} Since last many years, researchers are developing Mg/Al as well as Ca/Al and mixed metal-based HTs materials using various synthesis routes and applied as heterogeneous catalytic materials for base catalyzed organic synthesis.^{108,109} Herein, such studies have been noted about the performance of HTs for the biodiesel production.

Xie et al. have developed calcined Mg/Al hydrotalcites as heterogeneous base catalyst by using coprecipitation method for transesterification process of soybean oil and

Table 3: Metal-oxides and mixed-metal oxides as heterogeneous catalysts for biodiesel production using esterification or transesterification reactions.

Sr. No.	Catalysts	Esterification/trans-esterification reactions molar ratio of oil: alcohol	Ref.
1	Sulphated zinc oxide (SO_4^{2-} -ZnO and SO_4^{2-} /ZnO prepared by coprecipitation and impregnation method respectively	Transesterification of soybean oil Oil: methanol = 6:1	73
2	Lithium-doped ZnO prepared by using impregnation method followed by calcinations	Transesterification of vegetable oil Oil: methanol = 1:12	74
3	CaO-MoO ₃ -SBA-15 prepared by incipient impregnation method	Transesterification of soybean oil Oil: methanol = 1:50	75
4	Sulfated Fe ₂ O ₃ -TiO ₂ using conc. H ₂ SO ₄	Esterification of vegetable oil Oil: methanol = 1:20	76
5	Strontium and nickel- oxides prepared by using a co-precipitation method	Transesterification using macaw palm oil Oil: methanol = 1:9	77
6	Cu-nanoparticles impregnated in porous carbon support	Transesterification of pail oil/animal fat Oil: methanol = 1:10	78
7	Dual-acid catalyst sulfur-rich graphene oxide prepared by simple modified Hummer's method	Esterification of oleic acid with methanol Acid: methanol = 20:50 (w/w; g)	79
8	Alkali earth metal oxides (CaO, MgO and BaO) doped SiO ₂	Transesterification of vegetable oil/animal fat oil: methanol = 1:16	81
9	Calcium oxide derived from mud clam shell	Transesterification of castor oil Oil: methanol = 1:14	92
10	Ca-doped Ce-incorporated SBA-15 impregnated with CaO. (CaO/CeO ₂ and CaO-CeO ₂ /SBA-15)	Transesterification of palm oil Oil: methanol = 1:20	93
11	SrO-CaO mixed metal oxides	Transesterification of <i>Jatropha</i> oil Oil: methanol = 1:10	94
12	CaO/La ₂ O ₃ prepared by co-precipitation method	Transesterification of crude <i>Jatropha</i> oil Oil: methanol = 1:25	95
13	Acid-base bi-functional metal-boron catalysts prepared by sol-gel method (metal = Ca ²⁺ , Al ³⁺ , Mg ²⁺ , Zr ⁴⁺)	Transesterification of crude <i>Jatropha</i> oil Oil: methanol = 1:20	96
14	Mixed metal oxides (CaO-MgO, CaO-ZnO, CaO-La ₂ O ₃ and MgO-ZnO)	Transesterification of high acid <i>Jatropha</i> Oil: methanol = 1:25	97
15	Metal oxides (Co ₃ O ₄ , KOH, MoO ₃ , NiO, V ₂ O ₅ and ZnO)	Transesterification vegetable oil with excess methanol	98

Table 3: (continued)

Sr. No.	Catalysts	Esterification/trans-esterification reactions molar ratio of oil: alcohol	Ref.
16	NaY zeolite-supported La ₂ O ₃	Transesterification of castor oil. Oil: methanol = 1:25	102
17	Alkaline earth metal oxides (BaO, CaO, MgO and SrO)	Transesterification of palm oil Oil: methanol = 1:3 –1:15 (% w/w)	103
18	CsHPW ₁₂ O ₄₀ , Nb ₂ O ₅ , sulfated titania (TiO ₂ /SO ₄ ²⁻), sulfated zirconia (ZrO ₂ /SO ₄ ²⁻) and SnO ₂ /SO ₄ ²⁻	Esterification of dodecanoic (lauric) acid with methanol, propanol, 2-ethylhexanol Acid: alcohol = 1:1 up to 1:5	104
19	ZnO/zeolite and PbO/zeolite prepared by hydrothermal impregnation precipitation method	Transesterification of <i>Jatropha curcas</i> and <i>Pongamia pinnata</i> oil Oil: methanol (excess) = 1:>3	105

methanol to produce FAME through optimization of reaction conditions.¹¹⁰ The catalyst calcined at 500 °C with Mg/Al ratio of 3.0 found to be most active having higher basicity and suitable for the reaction having ~67 % FAME conversion. Yagiz et al.¹¹¹ have studied catalytic performances of the lipase enzyme immobilized hydrotalcites prepared by co-precipitation method by using commercial zeolites as immobilization materials. The obtained immobilized lipase materials have been used for transesterification reaction of oil. As results, HT was found to be the suitable supporting material for lipase than the other four types of zeolites used and it observed to be able to catalyze the transesterification of waste cooking oil with methanol to produce methyl esters.¹¹¹ Mg/Al hydrotalcites prepared by co-precipitation of Mg²⁺ and Al³⁺ ions in alkaline solution of NaOH followed by calcination at 400 °C.¹¹² The prepared catalyst used biodiesel production from pongamia oil with methanol through transesterification under optimized reaction conditions and resulted ~90 % yield of pongamia oil methyl ester showing potential activity of the present catalyst.¹¹² The hydrotalcites catalyst with Mg/Al molar ratio of 3.0, calcined at 450 °C under argon (Ar) flow for 6 h has been characterized for spectral analysis.¹¹³ The prepared material has been tested for transesterification reaction of soybean oil with methanol under mild conditions of temperature and pressure to produce biodiesel. The results show highest fatty acid methyl ester conversion of ~94 % at optimized reaction conditions which makes material to be a promising heterogeneous base catalyst for biodiesel formation.¹¹³ Chelladurai et al.¹¹⁴ have studied an environmentally benign process for the transesterification reaction of neem oil with methanol to

yield fatty acid methyl esters (FAME) using Zn–Mg–Al hydrotalcites as heterogeneous solid base catalysts thorough optimization of reaction conditions. The obtained highest triglyceride conversion rate was ~92 % at optimized conditions and this could be attributed to the incorporation of Zn into the Mg–Al hydrotalcite material.

Diserio et al.¹¹⁵ have reported catalytic performances of Mg/Al hydrotalcites (Pural®MG76) for biodiesel production through transesterification of soybean oil with methanol using both an autoclave and continuous packed bed reactor. The observations confirmed about the calcined Mg/Al hydrotalcites as effective heterogeneous catalyst for the transesterification of triglycerides with methanol where the used catalysts could be regenerated by washing with acetone and reused for the economical way without loss of significant performance.¹¹⁵ Costarrosa et al.¹¹⁶ have studied influences of the reaction parameters in terms of response surface methodology (RSM) for the heterogeneous transesterification of waste cooking oil with methanol to produce biodiesel using calcined Mg–Al hydrotalcite catalyst. The study has proved RSM as good indicative tool for predicting the biodiesel yield and also about the calcined Mg/Al hydrotalcites as an effective basic catalyst for the production of biodiesel from waste cooking oil.¹¹⁶ Mg/Al hydrotalcites has been synthesized by urea hydrolysis and co-precipitation methods and characterized.¹¹⁷ The prepared material tested for transesterification process of waste cooking oil (a triglyceride) with methanol and optimized the reaction conditions using hexane and glycerol as co-solvents. At optimized reaction condition, Mg/Al hydrotalcites as solid base catalyst gives maximum biodiesel yield and compared with the results of KOH as liquid homogeneous base catalyst.¹¹⁷ A series of solid base catalysts, KF-doped three-metal mixed hydrotalcites (KF/Ca–Mg–Al) with different cation ratio have been synthesized and applied in transesterification process of palm oil with methanol to yield FAME.¹¹⁸ The doping of KF and synergetic effect of Ca^{2+} and Mg^{2+} broadly improved the catalytic activity of the HT catalysts. As results, the prepared three-metal mixed hydrotalcites found to be highly active for biodiesel production and obtained ~99 % FAME yield at optimized reaction conditions.¹¹⁸ The spent catalysts could be regenerated and reused in the transesterification reaction where the FAME yield decreased apparently compared to fresh catalyst due to the fact that the layer structure of the catalyst helped raise the activity of the catalyst.

The Mg/Al based catalysts (double oxides of Mg and Al) prepared by coprecipitation method and characterized for structural properties.¹¹⁹ The formed double lamellar hydroxides followed by calcination gives double oxides show interesting catalyst properties such as a large

superficial area, synergic effect between its elements (which favors the development of the its basic characteristics) and also a shape memory effect, which allows the regeneration of the original structure. The prepared catalysts have been tested through heterogeneous catalytic transesterification reaction of vegetable oil with methanol and resulted in ~97 % FAME formation. The study shows the potential use of the MgAl based hydrotalcites for the biodiesel production and suggesting further structural modification for the improved catalytic activity.¹¹⁹ Mg/Al hydrotalcites doped with lanthanum and zinc cations with different amounts prepared by using co-precipitation method followed by calcination and the materials have been used as solid base catalyst in transesterification of soybean oil with methanol and *n*-octanol for biodiesel and biolubricants production respectively.¹²⁰ The transesterification reaction of canola oil with methanol has been reported using Mg/Al hydrotalcites heterogeneous solid base catalyst prepared by coprecipitation method followed by calcination.¹²¹ The results of the catalytic reaction have been compared with KOH as conventional homogeneous catalyst where the present catalyst found to be less active than KOH.

The potential contribution of Mg/Al hydrotalcites prepared through layered double hydroxide has been reported for the biodiesel production using transesterification of triglycerides.¹²² The interesting physico-chemical characteristics such as texture and surface morphology as well as basicity of the prepared materials could be modified through synthesis routes and chemical composition. The present report shows useful catalytic characteristic of the hydrotalcites as mixture of mixed oxides catalysts and as supports of active species like alkaline and alkaline earth metals compound.¹²² Simonetti et al. have reported use of Ca/Al based hydrotalcites catalysts prepared by impregnation method using KOH solution followed by calcination for the transesterification reaction of soybean oil in methanol and ethanol to produce biodiesel.¹⁰⁸ The catalytic performance of impregnated and non-impregnated catalysts has been compared for the transesterification reaction and as a result, the non-impregnated exhibited with higher activity and hence better performances due to availability of active sites used in the transesterification process.¹⁰⁸ Mg/Al hydrotalcites prepared by co-precipitation followed by calcination and loaded with K_2CO_3 .¹²³ The obtained material used as solid base catalyst for transesterification reaction of *Jatropha curcas* oil with methanol to produce FAME. In the study, spectral analysis confirmed the metal oxide formation which makes catalyst to be highly active and it could produce about ~96 % yield of biodiesel (FAME)

under optimized reaction condition.¹²³ Xue et al.¹²⁴ have synthesized activated Mg/Al hydrotalcites NPs by co-precipitation and hydrothermal activation with aqueous $\text{Ca}(\text{OH})_2$ solution and characterized its catalytic properties.¹²⁴ The prepared Ca-hydrotalcite contained both acidic and basic active sites due to which it could be used for esterification and transesterification of different oils with high acid value. The results show high catalytic activity for production of biodiesel (~93 % yield) from crude oils with high acid value without pretreatment.¹²⁴

Table 4 highlighting the use of various HTs as heterogeneous base catalysts for biodiesel production

Table 4: Hydrotalcites (HTs) as heterogeneous base catalysts for biodiesel production using esterification or transesterification reactions.

Sr. No.	HTs as base catalysts	Esterification/trans-esterification reactions molar ratio of oil: alcohol	Ref.
1	Ca/Al based HTs (Ca/Al ratio of 2:0) prepared by impregnation method using KOH solution	Transesterification of soybean oil Oil: methanol/Ethanol = 1:30 (~90–95 % FAME conversion)	¹⁰⁸
2	Calcined Mg/Al HTs prepared by coprecipitation using alkaline solution	Transesterification process of soybean oil Oil: methanol = 15:1 (~67 % FAME conversion)	¹¹⁰
3	HT-immobilized and zeolites-immobilized lipase enzymatic materials	Transesterification waste cooking oil Oil: methanol = 1:4 (~91 % FAME conversion)	¹¹¹
4	Calcined Mg/Al HTs prepared by coprecipitation using alkaline solution	Transesterification pongamia oil Oil: methanol = 1:6 (~90 % yield of pongamia oil methyl ester)	¹¹²
5	Calcined Mg/Al HTs under Ar flow (Mg/Al ratio of 3.0) prepared by coprecipitation using alkaline solution	Transesterification of soybean oil Oil: methanol = 1:20 (~94 % FAME conversion)	¹¹³
6	Calcined Zn–Mg–Al HTs	Transesterification reaction of neem oil Oil: methanol = 1:10 (~91 % FAME conversion)	¹¹⁴
7	Mg/Al HTs (Pural©MG76)	Transesterification of soybean oil in autoclave and in a continuous packed bed reactor Oil: methanol = 160 g :160 g (w/w) (~80–85 % FAME conversion)	¹¹⁵
8	Calcined Mg/Al HTs (Mg/Al ratio of 3.1) prepared by coprecipitation using alkaline solution	Transesterification of waste cooking oil Oil: methanol = 1:8 (~95–98 % FAME conversion)	¹¹⁶

Table 4: (continued)

Sr. No.	HTs as base catalysts	Esterification/trans-esterification reactions molar ratio of oil: alcohol	Ref.
9	Calcined Mg/Al HTs (Mg/Al ratio of 3.1) prepared by urea hydrolysis and coprecipitation methods	Transesterification of waste cooking oil Oil: methanol = 1:6 (~78–96 % FAME conversion)	¹¹⁷
10	KF-doped three-metal mixed HTs (KF/Ca–Mg–Al)	Transesterification process of palm oil Oil: methanol = 1:12 (~99 % FAME conversion)	¹¹⁸
11	Calcined Mg/Al based double oxides of Mg and Al prepared by coprecipitation using NaOH solution	Transesterification of soybean oil Oil: methanol = 1:9 and 1:12 (~97 % FAME conversion)	¹¹⁹
12	Mg/Al HTs (Mg/Al ratio of 2.0) doped with lanthanum (La^{3+}) and zinc (Zn^{2+}) cations	Transesterification of soybean oil Oil: methanol = 1:15 (~97 % FAME conversion)	¹²⁰
13	Calcined Mg/Al HTs prepared by coprecipitation using alkaline solution	Transesterification of canola oil Oil: methanol = 1:6 and 1:12 (~71 % FAME conversion)	¹²¹
14	Mg/Al HTs (Mg/Al ratio of 2:3) prepared by layered double hydroxide	Transesterification of triglycerides Oil: methanol = 1:12 (~96 % FAME conversion)	¹²²
15	Calcined K_2CO_3 loaded Mg/Al HTs (Mg/Al ratio of 3:1) prepared by coprecipitation using alkaline solution	Transesterification of <i>Jatropha curcas</i> oil Oil: methanol = 1:6 and 1:12 (~96 % FAME conversion)	¹²³
16	Mg/Al hydrotalcites NPs by coprecipitation and hydrothermal activation with aqueous $\text{Ca}(\text{OH})_2$	Transesterification of <i>Jatropha curcas</i> oil Oil: methanol = 1:30 (~93 % FAME conversion)	¹²⁴

through esterification or transesterification process of oil with methanol/ethanol using optimization of oil to alcohol molar ratio.^{108–124}

Metal Organic Frameworks (MOFs): MOFs are porous materials, composed of metal sites and organic linkers, have become a research hotspot due to their exceptional advantages, such as versatile synthetic strategies for controlled morphology, abundant pores, and high surface area.¹²⁵ These properties grant MOFs versatile functionalities, which have attracted significant interest from the scientific community in recent years.¹²⁵ Their crystalline-to-amorphous nature, consisting of metal ions or clusters linked to organic ligands, offers remarkable surface areas, a high degree of structural diversity, and tunable porosity, making them ideal for a wide range of applications.¹²⁵

With the advantageous character of polyporous materials, MOFs have gained the most suitability for biodiesel synthesis.¹²⁶ Molybdenum-MOFs has been synthesized by solvothermal method and applied as catalyst in the esterification reactions of oleic acid and palmitic acid to obtain biodiesel.¹²⁷ As a result, a 95 % yield was achieved with the fresh Mo-MOFs, and it was successfully recycled for four cycles, maintaining ~92 % efficiency. A hydrothermal synthesis of chromium(III) nitrate nonahydrate salt with EDTA as an organic ligand has been reported to prepare Cr(III)-EDTA MOF, which demonstrates efficient and promising performance for the esterification of oleic and palmitic acids under mild reaction conditions.¹²⁸ Copper(II) based MOFs, Cu-benzenedicarboxylic acid (Cu-BDC), Cu-benzenetricarboxylic acid (Cu-BTC) and MOF-74, provide many active sites that act as Lewis acid species and therefore, used as catalysts in the esterification process of waste cooking oil.¹²⁹ The synthesis of 75 % and 50 % oil content with Cu-BDC catalyst converted in FFA content of 5.49 % and 4.826 %, respectively.

2.2 Hydrogen production

Hydrogen (H_2), as a fuel and one of the most extensively studied substitute energy resources for available sources those are being consumed rapidly.^{130,131} The combustion of hydrogen can be considered as environmentally benign because it produces only water as by-product, and its adoption as fuel in internal combustion engines, would lead to a remarkable reduction in atmospheric pollution.¹³² Now days, hydrogen-based technologies are being proposed for having economically and environmentally efficient system to produce hydrogen such as photo-catalytic water-splitting,^{133–137} hydrocarbon decomposition,^{138,139} photo-reforming^{140–144} aqueous phase reforming,^{145–150} and auto-thermal/oxidative steam reforming.^{151–153} In this view, mono-metallic, bi-metallic or poly-metallic heterogeneous catalysts based on NPs (oxide supported) are well established catalytic systems for hydrogen production. Several Pd, Pt, Ru, Rh-based heterogeneous catalysts with comparable hydrogen production rate have been reported.

Santo et al.¹³² have reviewed the specific catalytic applications of reforming processes such as steam, auto-thermal/oxidative steam, aqueous phase and dry reforming, catalytic partial oxidations, decomposition, photocatalytic water-splitting and photo-reforming reactions. The authors have reported heterogeneous catalysis based on supported bimetallic NPs, to the reactions favorable for the hydrogen production from the renewable raw materials.¹³² They have discussed on advantageous applications of bimetallic versus

monometallic catalytic systems, as well as focused on characterizations of structural properties. The correlation between structure and catalytic properties has an influence on the promoter addition. The potential of bimetallic catalyst NPs could be seen from the number of examples of the industrial applications significantly such as hydrogen production using photo-reforming and photocatalytic water-splitting those are discussed in the present article.¹³²

Furthermore, metal-supported heterogeneous catalysts can induce changes in the electronic properties of the catalyst surface, offering numerous opportunities for developing advanced catalysts with enhanced catalytic performance.²⁶ The noble metal catalysts are also interesting aspects of catalysis for hydrogen production through HER because of their ΔG_{H^*} is closed to zero.¹⁵⁴ Zhou et al. have related the catalytic activity with the electronic structure and chemical composition of noble metal-based electrocatalysts.¹⁵⁴ In continuation, a series of lanthanum based heterogeneous catalysts of 1 wt% Pt/LaMO₃ where M = Al, Cr, Mn, Fe, Co, Ni has been synthesized and used in the catalytic study of aqueous phase reforming of waste biomass, such as glycerol for sustainable hydrogen production.¹⁵⁵

Nagaoka et al.¹⁵⁶ have demonstrated hydrogen production by oxidative decomposition of ammonia at room temperature to an acidic RuO₂/γ-Al₂O₃ catalyst. In the study ammonia chemisorbed onto RuO₂/γ-Al₂O₃ catalyst which further increased the amount of the multilayer physisorbed ammonia which causes strong heat evolution that enables to initiate the oxidative decomposition of the ammonia onto large surface of RuO₂ NPs. The authors have measured and compared the autoignition temperatures of the RuO₂/γ-Al₂O₃ and RuO₂/γ-La₂O₃ catalysts.¹⁵⁶ As results, on ammonia and oxygen supply to the catalyst at room temperature, it has produced hydrogen along with nitrogen and water vapor. The process requires neither an external energy source nor the use of any complex procedures. The present study briefly introduces a conceptual idea of self-heating of catalysts by adsorption of reactant molecules which is a novel strategy for the cold-start process for hydrogen production from ammonia and other reactions.

Recently, a study discussed the progress and challenges in using non-noble metal cobalt-based heterogeneous supported catalysts, particularly carbon materials, metal oxides, MOFs, and nickel foams, for hydrogen generation from ammonia borane.¹⁵⁷ It provides insights into how the preparation of the electronic and spatial structures of Co-based catalysts can significantly influence the decomposition of ammonia borane for hydrogen generation.¹⁵⁷ Brack et al.¹⁵⁸ have introduced heterogeneous catalysis for the hydrogen production from the hydrolysis process of sodium borohydride (NaBH₄). The authors have discussed about the

factors affecting the catalytic hydrolysis process of aqueous solution of NaBH_4 such as catalyst role, reaction conditions (temperature, time, concentration and volume of NaBH_4 and the used stabilizers). The article has brief discussion about the catalysts based on noble metals, mainly focus on Pt and Ru as most efficient at rapid production of hydrogen from the aqueous NaBH_4 solution. As noble-metal based catalysts resulting much expensive, transition metal-based particularly Co and Ni-based catalytic system would be a desirable alternative and much more work has been done for the hydrogen generation. Cobalt-borides are found to be emerging catalyst of choice due to low cost and simple synthesis procedures with high catalytic activity leading to maximum hydrogen production yields. They also have explained other transition metal-based as well as metal free-based heterogeneous catalysts for practical applications of the hydrogen generation.¹⁵⁸ Srifa et al.¹⁵⁹ also have studied hydrogen generation by ammonia decomposition using Cs-modified $\text{Co}_3\text{Mo}_3\text{N}$ catalysts prepared by a facile single-step decomposition of a mixture of hexamethylenetetramine and corresponding metal salts under the flow of nitrogen at 700 °C. The kinetic study of the catalytic process shows influence of the presence of the Cs species as it significantly enhanced the catalytic activity of $\text{Co}_3\text{Mo}_3\text{N}$, an excess amount of Cs could be reduced the activity and hence lower the H_2 production rate. The observed enhancement could be due to electronic modification of $\text{Co}_3\text{Mo}_3\text{N}$ by the electron donation of Cs promoter.¹⁵⁹

Yan et al.¹⁶⁰ have compared catalytic activities of Ni, Co and W with ZrO_2 support for hydrogen production from PEG-contaminated wastewater by supercritical water gasification process. The results of the analysis show Ni/ ZrO_2 exhibits highest hydrogen yields which could be due to catalyst inhibition of toxic intermediate production. The study demonstrated the promising use of Ni/ ZrO_2 as heterogeneous catalyst for hydrogen production in a supercritical water gasification process with high activity and stability.¹⁶⁰ Yuranov et al.¹⁶¹ have developed a heterogeneous catalytic reactor for continuous production of hydrogen via formic acid dehydrogenation. The catalyst support consisting of cross-linked polystyrene beads and polymer electrolyte fuel cell operated on $\text{H}_2 + \text{CO}_2$ mixtures to produce neat hydrogen. The model presented could help to use formic acid as hydrogen carrier medium and to make maximum industrial application for the sustainable technology. Yamashita et al.¹⁶² have addressed most relevant research approaches in hydrogen generation from two of the most promising hydrogen storage materials such as formic acid and ammonia-borane over carbon supported metal NPs based catalysts. The authors have highlighted recent advancement in mono-metallic and bi-metallic

Pd-based and Ru-based catalytic system, also discussed about the important features like nano-particle size, electronic features and composition, functionality of the support and influence of the used additives present in the medium. They have concluded about the prior meet of the high performance heterogeneous catalysts for the hydrogen production with efficiency, economic and reusability.¹⁶² The authors also have reported design and development of efficient Pd-based heterogeneous catalysts supported on carbon or carbon containing materials for the formic acid dehydration process in liquid phase for hydrogen production.¹⁶³ They have described important features of metal active phase and catalytic support for finding the efficient catalyst under the optimum experimental conditions. The main issue has been noted about the stability of the catalyst which has to be improved for the practical applications. In this context, modulating the nanoparticle-support interaction could be of great significance in achieving catalysts with notable stability. The incorporation of an adequate heteroatom through doping in the carbon material could be an effective tool to form interesting catalytic system for the current demand through appropriate surface fictionalization. Another way of modification in the synthesis route so that porosity of the carbon material support could be utilized in anchoring and dispersing the metallic active phase would be effective work of interest through which active and durable catalytic system could be developed, and searching useful capping agent to inhibit the nano-particle sintering under using experimental conditions. Also, they have concluded about future investigation to be initiated the use of non-noble metallic NPs as cost effective and durable active catalysts for the hydrogen production from dehydrogenation of the formic acid.¹⁶³ Yamaguchi et al.¹⁶⁴ have reported gaseous fuel production from non-recyclable paper wastes such as shredded documents and paper sludge over supported metal catalysts. The gasification catalytic reactions show, a charcoal-supported ruthenium (Ru/C) catalyst found to most active and among to the metal used, the order of the catalytic activity was found to be $\text{Ru} > \text{Rh} > \text{Pt}$. The gas fuel yield increases by ball-milling treatment of the recycled paper and cellulose powder.¹⁶⁴ The present conceptual technique indicating the possibility of fuel gas production from paper wastes in high-temperature liquid water.

Sikander et al.¹⁶⁵ have introduced scientific approaches reported by researchers for the hydrogen production using HTs based catalysts through describing synthesis methods and structural properties. The authors have briefly explained co-precipitation, urea hydrolysis, microwave treatment and sol-gel method of synthesis for HTs. Various methods of hydrogen production have been discussed such

as steam reforming of methane, methanol, ethanol and dry hydrocarbons and partial oxidation of methane. The catalysts, HTs are observed to be more active in almost all hydrogen production processes because of high surface area. Furthermore, the compositional ratios of active metallic cations along with their interaction with the interlayers are a key role for catalytic efficiency.^{166,167} Doping of element is another way to enhance the catalytic performance where use of noble metals (Pd,^{168,169} Pt,¹⁷⁰ Rh¹⁷¹) have been reported successfully. The rigorous operating conditions of hydrogen production processes could damage structural properties of the catalyst, sintering of the cations and deactivation of the catalyst also affects the catalytic efficiency of the HTs. The authors also have developed double layered HT based Mg–Ni–Al catalyst using co-precipitation method by varying Ni content and studied its catalytic performance for the hydrogen production through methane decomposition.¹⁷² The nickel concentration has not been effective to the overall methane decomposition reactions due to the sintering of active sites species leads to depriving of the overall rate of methane conversion. The used catalyst support have played a typical role in the diffusion of the deposited carbon, resulted improved the overall performance rate.

Three metal-based HTs (Ni/Zn/Al-HT) with different Ni/Zn ratios have been prepared by a coprecipitation method and characterized for structural properties where HT and ZnO phases observed along with Zn²⁺ into the layer.¹⁴⁵ The prepared material has been used for hydrogen production via aqueous phase reforming of ethylene glycol and resulting high H₂ generation rate with high selectivity.¹⁴⁵ Ni–Fe mixed oxides obtained from reevesite, a HTs type material prepared by co-precipitation method and tested for steam reforming of ethanol for hydrogen production.¹⁴⁵ The comparative performance of hybrid materials comprising a Ni-based reforming catalyst and HT (Ni-HT) or calcium based sorbents (Ni–CaO/Al₂O₃) has been reported for sorption-enhanced steam methane reforming for H₂ production.¹⁷³ The prepared hybrid material (Ni-HTs) exhibited with superior adsorption characteristics and stability compared to powdered mixtures of commercial Ni/Al₂O₃ catalyst and the respective sorbent (CaO).¹⁷⁴ He et al.¹⁷⁵ have studied catalytic performances of noble-metal free-catalyst obtained from Ni/Al HTs for hydrogen production through hydrous hydrazine (N₂H₄·H₂O) decomposition and compared with the ~78 wt % Ni/Al₂O₃-IMP sample. The results show that supported Ni catalyst with a high loading and good dispersion exhibits ~100 % conversion and ~93 % H₂ selectivity for the N₂H₄·H₂O decomposition at room temperature. The observed activity is due to the cooperation

of Ni NPs and strong basic sites which make catalyst as a promising candidate to replace noble-metals for hydrogen production under ambient conditions.¹⁷⁴ Homsi et al.¹⁷⁶ have prepared Co-based HTs (Co₆Al₂ oxide) and thermally stabilized and impregnated using metal precursors of Cu and Ru followed by calcination. The characterization results show formation of CuO, RuO₂, Co₃O₄ and CoAl₂O₄ after calcination of the impregnated materials. Both, impregnated and non-impregnated samples have been used for the steam-reforming of the ethanol for H₂ production.¹⁷⁶ As results, Ru with impregnated samples exhibit high catalytic activity compared to Cu-impregnated sample which is attributed to the formation of easily reducible Ru and Co-oxide species at the surface of the support.¹⁷⁶ The authors also have studied catalytic performances of Cu/Co–Mg–Al-based catalysts in the ethanol steam reforming reaction under atmospheric pressure in a fixed catalytic bed reactor coupled to a micro-gas chromatography.¹⁷⁷ From the reaction, H₂ and CO₂ evolved and it increased with the cobalt content and 5Cu/Co₆Al₂ gives very good conversion of H₂ and CO₂. The presence of copper as an active phase has improved ethanol conversion and H₂ production compared to the results obtained in the case of the supports alone. The study leads to develop a catalyst operate at low temperature with high selectivity to avoid formation of by-products.¹⁷⁷ Tuza et al.¹⁷⁸ have reported hydrogen production by aqueous-phase reforming of glycerol using Ni/Cu catalysts derived from HT precursors. The obtained materials have been characterized for structural and surface properties. A clear improvement in the orderliness of the layer has been noted with decreasing copper content and samples with higher amount of copper have larger BET surface areas. The Ni-catalyst without Cu shows high catalytic glycerol conversion observed with good H₂ selectivity and Ni₅Cu catalyst also shows high H₂ selectivity with the smallest amount of CO and CH₄.¹⁷⁸

The compositional variation and structural advantages such as highly ordered and tunable metal nodes and organic linkers, MOFs enable rapid ion transport and high capacitance. With their abundance of active energy storage sites, MOFs have emerged as attractive candidates to meet the demands of next-generation energy storage technologies in batteries and supercapacitors.^{125c} MOFs and their nanocomposites have been widely synthesized, particularly for their potential applications as hydrogen storage materials in proton exchange membrane fuel cells (PEMFCs).¹⁷⁹ MOFs are also of interest as potential materials for use as electrode in lithium, zinc and sodium-ion batteries.¹⁸⁰

The catalysts used in the hydrogen production process have been summarized^{26,132,145,154–182} in Table 5.

Table 5: Hydrogen production using various catalysts.

Sr. No.	Catalysts	Catalytic process	Ref.
1	Supported bimetallic NPs	Photo-reforming and photocatalytic water-splitting	132
2	Acidic RuO ₂ /γ-Al ₂ O ₃ catalyst	oxidative decomposition of ammonia	156
2	1 wt% Pt/LaMO ₃ where M = Al, Cr, Mn, Fe, Co, Ni prepared by harsh hydrothermal conditions	Aqueous phase reforming of waste biomass	157
3	Noble-metal (Pt, Ru and Rh), transition metal (Ni and Co) based catalysts	Hydrolysis process of sodium borohydride	158
4	Cs-modified Co ₃ Mo ₃ N	Ammonia decomposition	159
5	Ni, Co and W with ZrO ₂ support (Ni/ZrO ₂ , Co/ZrO ₂ , W/ZrO ₂)	PEG-contaminated wastewater by supercritical water gasification process.	160
6	Different active Ru complexes supports on zeolite ZSM-5, mesoporous MCM-41 silica and functionalized polystyrene beads	Formic acid dehydrogenation	161
7	Monometallic and bimetallic Pd-based catalytic systems, (Pd, Pd/Ag, Pd/Au)	Formic acid dehydrogenation	162
8	Carbon supported metal NPs	Dehydrogenation of formic acid and ammonia-borane	163
9	Charcoal-supported ruthenium (Ru/C)	Gasification catalytic reactions (gaseous fuel production from non-recyclable paper wastes)	164
10	Hydrotalcite (HTs) consisting of different metals like Fe, Ni, Cu, Pt	Steam reforming of methane, methanol, ethanol and dry hydrocarbons and partial oxidation of methane	165
11	Ce-promoted Ni/Mg–Al catalysts	Dry reforming of methane	166
12	HTs supported Pd ₂ Ga and PdZn intermetallic NPs	Methanol steam reforming	168
13	PdZnAl-HTs supported catalyst	Oxidative methanol steam reforming	169
14	Ni, Co and Pt/hydrotalcites-WO _x	Ethanol steam reforming	170
15	Rh-doped Ni/Mg(Al)O catalysts	Methane steam reforming	171
16	Double layered HT based Mg–Ni–Al	Methane decomposition	172
17	Ni/Zn/Al derived HTs	Aqueous-phase reforming of ethylene glycol	145
18	HTs- and calcium-based hybrid materials	Methane steam reforming	173
19	Ni/Fe derived HTs	Ethanol steam reforming	174
20	Noble-metal-free catalyst derived from Ni–Al HTs	Hydrazine (N ₂ H ₄ ·H ₂ O) decomposition	175
21	Ru and Cu supported HTs	Methane steam reforming	176
22	Cu/Co–Mg–Al-based catalysts prepared by HTs route (5Cu/Co ₆ Al ₂)	Ethanol steam reforming	177

Table 5: (continued)

Sr. No.	Catalysts	Catalytic process	Ref.
23	Ni and Cu supported HTs	Aqueous-phase reforming of glycerol	178
24	Prussian blue analogues	Hydrolysis of NaBH ₄	181
25	Fluorine-doped NiO and Ni@C prepared through organic-inorganic hybrid approach	Urea oxidation reaction	182

3 Environmental applications

Currently, the problem associated to the energy and environment has no universal solution to solve it. Most of human activities and more, rapidly increasing population and thus, even faster increasing global energy consumption and environmental burdens lead to generate the said unsolved problems. Many more awareness and progressively efforts are being applied to improve the efficiency and accessibility of environmental remediation and Green Chemistry processes. Environmental catalysis certainly plays a typical role in the design and development of efficient processes and technologies to reduce or to minimize waste generation throughout saving energy.¹⁸³ Herein, different heterogeneous catalytic systems have been discussed to understand relation between the structure/chemistry and the performance in heterogeneous catalysis which would help to design novel efficient materials for addressing the challenges in potential applications for environmental remediation. These include metal-based and/or metal-free-based catalysts and carbon-based catalysts for green chemistry, semiconductors-based catalysts for photocatalysis and other catalytic systems for environmental technologies.

3.1 Carbon dioxide (CO₂) reduction

Faster deforestation makes sudden increment of CO₂ concentration in atmosphere and thus, global warming problem and climate change become the interest of attention.¹⁵⁰ Therefore, now it is become necessary to find out a significant alternative to capture CO₂ and convert it into useful chemicals and sources of fuel.¹⁸³ The availability of the alternative energy source is connected to the source of hydrogen which is carbon neutral and economically feasible. In this view, the hydrogenation of CO₂ to methanol synthesis is providing a renewable or sustainable source of hydrogen.

There has been focused research work on finding selective catalyst that can capture or convert through CO₂ activation under mild reaction conditions with maximum selectivity and yield of methanol. Bahruji et al.¹⁸⁴ have studied structure activity relationship of two series of Pd/ZnO catalysts prepared by immobilization and impregnation methods for direct hydrogenation of CO₂ to methanol. As results, different performances observed for both catalysts prepared by different methods. Pd-NPs deposited through sol-immobilization method which produced active Pd/ZnO NPs catalysts with controlled particle size. It is observed that, high Pd loadings for colloidal catalysts increases methanol formation due to Pd–Zn bimetallic formation and also, methanol production could be reduced at higher temperature due to some sintering effect.¹⁸⁴ A multicomponent Cs-doped CuO–Fe₂O₃ supported on Al₂O₃ (Fe–Cu–Cs/Al₂O₃) catalyst has been reported for chemical CO₂ recycling by reverse water-gas shift (RWGS) reaction and compared its catalytic activity with that of Fe/Al₂O₃, Fe–Cu/Al₂O₃ and Fe–Cs/Al₂O₃ catalysts.¹⁸⁵ The addition of Cu to the bare Fe/Al₂O₃ catalyst enhances the activity and selectivity because of Cu–Fe effect and reduced sintering. Similarly, addition of Cs promoter affects the catalytic activity of Cu–Fe/Al₂O₃ and thus, multicomponent catalyst Cs–Fe–Cu/Al₂O₃ has highest level of CO₂ conversion with full selectivity to CO formation at low temperature. The study reveals the role of promoter added to the catalysts, Cs helps in CO₂ activation due to its basic character in nature through ease of electron transfer from the catalyst to the reactants and facilitation CO₂ adsorption on the catalyst surface. Addition of promoter also helps to suppress the methanation process and it could improve selectivity towards desired product.¹⁸⁵ The study concluding about unexceptional stability and selectivity could be gained through Cs-doped heterogeneous catalytic materials and it suggests using of such materials in gas phase chemical CO₂ recycling. The authors have reported multicomponent Ni-based catalysts supported on Al₂O₃ promoted by the addition of Sn and CeO₂ for the catalytic conversion of CO₂.¹⁸⁵ The results also favoring the earlier study as addition of Sn and CeO₂ promoters have improved the catalytic activity of Ni/Al₂O₃ through enhancement of CO₂ adsorption on the catalyst surface. The presence of CeO₂ enhances the oxygen storage capacity and modified acid/base characteristics of the support lead to improve catalytic behavior over a range of temperatures and space velocities. The catalytic system has also been applied to bi-reforming of methane reaction and significant conversion with stability was observed.¹⁸⁶ The study conducted provides a strategy to design and develop efficient and economic catalyst for practical syngas production from CO₂/CH₄ mixtures. Mutz et al.¹⁸⁷ have prepared bimetallic Ni₃Fe catalyst supported

on γ -Al₂O₃ using homogeneous deposition-precipitation method for application in CO₂ methanation and correlate performance and structure of the catalyst. Spectral analysis shows, formation of Ni₃Fe alloy with high fraction of Ni and Fe resulting into small and well defined NPs with controlled particle size and good dispersion. The catalytic performance of the prepared Ni₃Fe has been compared with that of monometallic catalyst of Ni by using a micro-channel packed bed reactor under industrially relevant reaction conditions. As results, Ni₃Fe exhibited with improved performance to have conversion of CO₂ about ~71 % selectively for methanol production and most important about retained a high stability. The study indicating importance of synergetic effect of Ni and Fe due to which catalyst has excellent performance and stability.¹⁸⁷ Cobalt catalysts supported on ZrO₂ (Co/ZrO₂) and Al₂O₃ (Co/Al₂O₃) prepared by impregnation with different metal loadings show good catalytic activity for CO₂ methanation.¹⁸⁸

Veselovskaya et al.¹⁸⁹ have studied direct air capture/methanation process over the commercial nickel methanation catalyst NKM-2V which is effectively combine CO₂ capture from ambient air and convert it into methane by Sabatier reaction. The experimental analysis showing enhancement of CO₂ to CH₄ conversion with increase of temperature and decrease in CO₂:H₂ ratio. The Sabatier process also performed well in the two reactor system using K₂CO₃/Al₂O₃ material for direct capture of CO₂ from ambient air and the commercial nickel catalyst for methanation of CO₂ via Sabatier process. Wu et al.¹⁹⁰ have studied influence of formate (HCOO[−]) coverage on the reaction rate of methanol synthesis from CO₂ hydrogenation over Cu (2 1 1) with the coverage-dependent adsorbate-adsorbate interactions. The study shows, increasing formate coverage would destabilize the adsorption of the reactant molecules/reaction intermediates and transition states. Turn over frequency varied at different coverage of surface species under the same reaction condition. The combination of HCOO and HCOOH hydrogenation steps could be a rate-determining step and thus, methanol formation could be controlled through surface coverage of formate and the effective free energy barriers.¹⁹⁰ Han et al.¹⁹¹ have prepared Au nano-clusters with different particle size (average ~2 nm) on various supports (ZnO, CeO₂, TiO₂, ZrO₂) and studied their catalytic performance on direct hydrogenation of CO₂ to methanol under solvent free condition. Among the all catalysts prepared, Au/ZrO₂ with 1.6 nm particle size exhibits highest catalytic activity and selectivity towards methanol formation at low temperature, mainly because of small particle size and appropriate coupling between the Au particles and support in the catalyst.¹⁹¹ Williams et al.¹⁹² have prepared unsupported bimetallic Pd–In NPs by using

thermal decomposition of Pd and In precursors in high boiling point solvent followed by reduction using dilute hydrogen gas. PdIn NPs catalyst has been tested for liquid phase methanol synthesis process and found to be most efficient catalyst showing ~70 % higher methanol production rates compared to conventional catalysts such as Cu/ZnO/Al₂O₃.¹⁹² Rao et al.¹⁹³ have studied fundamental physicochemical properties of CeO₂ to improve its catalytic activity for energy and environmental applications. In the study, shuttle-shaped CeO₂ prepared under hydrothermal condition by homogeneous precipitation method and the material shows good surface area and low temperature reducibility which show superior CO oxidation efficiency as environmental application. The linear sweep voltammetry, chronopotentiometry and CO stripping voltammetry studies show that CeO₂ provides higher number of labile OH_{ads} species through active triple-phase interfacial sites for facile oxidation of CO_{ads} on Pt/C as energy application.¹⁹³ The study set a significant potential and anti-poisoning effect of CeO₂ to Pt/C for electro-oxidation of ethanol in acidic media. Arena has reported the composite MnCeO_x system having high redox activity, surface amphoteric behavior and good chemical stability as a viable alternative to highly-cost noble metals for a variety of environmental catalytic applications.¹⁹⁴ These include a range of applications such as the detoxification treatment of industrial wastewater; the abatement of pollutants in gas exhausts; and bio-15 fuel and fine-chemicals synthesis manufacture.

Jadhav et al.¹⁹⁵ have discussed about the recent advanced studies of last decade on catalytic CO₂ hydrogenation to methanol. They have explained the importance of the various novel synthesis routes like solid-state reaction, ultra-nitrate combustion and reverses co-precipitation under ultrasound irradiation to prepare CuO/ZnO/ZrO₂ heterogeneous catalysts.¹⁹⁵ The main focus was CuO/ZnO-based catalyst promoted with Pd and Ga for CO₂ hydrogenation to methanol. As discussed earlier in the text, addition of Pd and Ga promoters enhances the catalytic activity, stability and selectivity of CuO/ZnO catalyst, i.e., Pd/ZnO¹⁹⁶ and Ga promoted Pd/SiO₂,¹⁹⁷ show excellent catalytic behavior. Authors also have discussed two pathways of catalytic hydrogenation of CO₂ to methanol; one is a RWGS and another, through mechanism of formate (HCOO⁻) intermediate formation.¹⁹⁵ They have concluded, among the available alternate catalytic techniques for methanol synthesis from CO₂ dehydrogenation via RWGS reaction would be promising tool. Porosoff et al.¹⁹⁸ have demonstrated the possible use of a low-cost non-noble metallic material Mo₂C (molybdenum carbide) as an active and selective heterogeneous catalyst for conversion of CO₂ using hydrogen. The spectral analysis shows that carbide is

preliminary active phase of Mo₂C while oxide form was observed throughout the reaction. Mo₂C catalyst has ability to break C=O bond of CO₂ and to dissociate hydrogen to either perform hydrogenation of CO₂ or remove oxygen from Mo₂Cz–O intermediate, thus, this way catalyst could show its dual functionalities which makes it suitable for CO₂ activation.¹⁹⁸ The present catalyst preparation is much lower cost make possible to set a large-scale catalytic CO₂ conversion process. Waclawek et al.² have discussed the mechanism of heterogeneous catalysis and advances in its development for environmental applications. They also have introduced a heterogeneous catalysis as an important aspect of the chemical process, from the synthesis methods and characterization techniques through surface morphology. The authors have highlighted the challenges about to improve spectroscopic and microscopic techniques to provide structural information such as chemical composition, size and shape of metal-NPs and gas phase concentrations in a spatially and time-resolved manner. They have suggested, industrial chemistry needs to combine all of these things together to understand the solid handling, chemical reaction, energy engineering, and heat and mass transfer of these catalytic processes. Theoretical scientist and physicist would have good partnership to make possible to design and develop superior catalytic systems for inexpensive fuel-cell vehicles.²

Yan et al.¹⁹⁹ have provided detailed overview of the development of nickel-based bimetallic catalysts for chemical and electrochemical processes such as catalytic reforming, dehydrogenation/hydrogenation and electrocatalysis for energy production and environmental remediation. The authors have discussed the role of bimetallic surface and each metal counterpart of the reactions, and the surface activity relationships which are typical part of catalytic performances. They have explained diffusion rate of Ni which is the major issues related to the catalyst activity and stability under the different reaction conditions like high temperature for reforming condition. On point of view, to develop cost effective catalysts without compromising their activity and stability, it could be possible by alternative way of introduction of non-metal elements such as boron and phosphorous and already nickel-borides and phosphides could further improves the catalytic behavior for the desired applications.¹⁹⁹ Labhasetwar et al.²⁰⁰ have studied a number of perovskites based on Co, Mn, Ru, and Fe and their substituted compositions. The prepared perovskites catalysts show good redox properties, the promotional effect of co-ions, and the increased exposure of catalytically active transition metals in certain preparations. The catalysts exhibited enhanced catalytic activity for diesel soot oxidation, three-way catalysis, NO decomposition, low-

temperature CO oxidation and oxidation of volatile organic compounds.²⁰⁰ Wang et al.²⁰¹ studied the physicochemical properties of fly ash exhibiting strong thermal stability and characteristic of a catalyst support. The fly ash supported catalysts have shown a very good heterogeneous catalytic activity for a variety of catalytic reactions as H₂ production, CO₂ reforming of methane, NH₃ decomposition, catalytic reduction of NO_x and SO_x, methane oxidation, dye decomposition, petroleum hydrocracking.²⁰¹

MOFs have also been reported to be efficient photocatalyst²⁰² and electrocatalysts²⁰³ for CO₂ capture. Cobalt–porphyrin MOF has been examined for selective reduction of carbon dioxide to carbon monoxide in aqueous electrolytes with the 76 % yield and stability over 7 h with a per-site turnover number of ~1,400.^{204b} A case study on Bi-based MOFs has been reported for electrochemical CO₂ reduction and as results excellent activity, selectivity, and durability for formate production.^{204c}

Table 6 contains various catalytic systems for CO₂ reduction^{184–206} as environmental application.

3.2 Degradation of organic pollutants

Rapidly developing industrial activities produce huge amount of organics containing non-degradable solid wastes which are spread out in the open environment and further contaminates groundwater and surface water as well as air. The major contamination produces from petroleum refining, petrochemicals, pharmaceuticals, dye, paper, plastic, dairy production, fertilization and pesticide chemical industries etc.^{207–209} Many reports are published related to develop effective process and technologies for wastewater treatment and oxidation process to decompose toxic and hazardous impurities at low cost and high efficiency. The literature on heterogeneous catalysis opens the ways about to use of novel catalytic systems for the decomposition of organic wastes from the aqueous solution as well as conversion of toxic gaseous pollutants to harmless products.

The most preferred catalytic systems are those based on photocatalysis with advanced oxidation processes (AOPs), as they offer the potential to utilize naturally available and renewable solar energy as a light source for photochemical waste remediation, making the process both green and sustainable.²⁰⁹ Among AOPs, semiconductor-mediated photocatalysis has proven to be highly effective, as it completely mineralizes contaminants present in either the gas or liquid phase.^{210,211} In these intriguing and effective fields of innovation, TiO₂ photocatalysis and the photo-Fenton process are

Table 6: Catalytic CO₂ reduction using various catalysts.

Sr. No.	Catalysts	Catalytic process	Ref.
1	Pd/ZnO	Direct hydrogenation of CO ₂ to methanol	180
2	Cs-doped CuO–Fe ₂ O ₃ supported on Al ₂ O ₃ (Fe–Cu–Cs/Al ₂ O ₃)	Reverse water-gas shift (RWGS) reaction	181
3	Ni-based catalysts supported on Al ₂ O ₃	Catalytic conversion of CO ₂ and bi-reforming of methane, syngas production form CO ₂ /CH ₄ mixtures	182
4	Ni ₃ Fe catalyst supported on γ-Al ₂ O ₃	CO ₂ methanation	183
5	Cobalt catalysts supported on ZrO ₂ (Co/ZrO ₂) and Al ₂ O ₃ (Co/Al ₂ O ₃)	CO ₂ methanation	184
6	Commercial nickel methanation catalyst NKM-2V	Direct air capture/methanation process	185
7	Cu(211)	Hydrogenation of CO ₂ to methanol	186
8	Au nano-clusters with different particle size (average ~2 nm) on various supports (ZnO, CeO ₂ , TiO ₂ , ZrO ₂)	Direct hydrogenation of CO ₂ to methanol	187
9	Unsupported bimetallic Pd–in NPs	Liquid phase methanol synthesis process	188
10	CeO ₂ (cerium oxide)	CO oxidation	189
11	Composite MnCeO _x	Redox process	190
12	Carbon nanotube-supported Pd/ZnO	Hydrogenation of CO ₂ to methanol	192
13	Ga promoted Pd/SiO ₂	Hydrogenation of CO ₂ to methanol	193
14	Mo ₂ C (molybdenum carbide)	Hydrogenation of CO ₂ to methanol	194
15	Nickel-based bimetallic catalysts	Hydrogenation of CO ₂ to methanol	195
16	Fly ash supported catalysts	CO ₂ reforming of methane	197
17	Cobalt–porphyrin MOFs	Selective reduction of carbon dioxide to carbon monoxide in aqueous	199
18	Bi-based MOFs	Electrochemical CO ₂ reduction	199
19	NNU-29 (polyoxometalate-based MOFs)	Photoconversion CO ₂ to formate	200
20	Postsynthetic exchange (PSE) of Ti(IV) into a Zr(IV)-based MOF	Photocatalytic CO ₂ reduction to HCOOH	201
21	Bimetallic (Zr/Ti)-MOFs	Photocatalytic CO ₂ reduction to HCOOH	202

two well-established AOPs. As a result, there are a significant number of literatures on their environmental applications, such as water and air decontamination, as well as self-cleaning surfaces.

Merouani et al. have explored the use of AOPs, particularly for environmental remediation, followed by photoactivated processes.^{14–17} In these studies, authors have developed a number of active radicals to facilitate the formation of reactive species for the degradation of toxic dyes such as chlorazol black,^{14a} Allura Red AC,^{14b} Safranin O,^{14c} textile dyes and organic contamination.¹⁵ The authors also applied the combined use of heterogeneous photocatalysis with high-frequency ultrasonic irradiation for dye and phenol degradation.^{16,17} It was observed that the solar photocatalytic process operated efficiently, even when the pollutant was present at high concentration levels. It could be attributed to the occurrences of synergistic effect strongly dependent on the initial substrate concentration.²¹²

Duan et al.²¹³ have discussed AOPs as effective technique for activating superoxides radicals for degradation of organic pollutants in aqueous systems. Magnetic (Fe_3O_4) carbon supported manganese oxides ($\text{Fe}_3\text{O}_4/\text{C}/\text{Mn}$) have been used as an effective catalytic system for phenol degradation through peroxymonosulfate (PMS) activation.²¹⁴ In the catalytic system, radical generation takes place due to redox process of $\text{Mn}^{4+}/\text{Mn}^{3+}$ and magnetic support helps for catalyst separation. The catalyst CoFe_2O_4 , prepared from Co–Fe alloys for the catalytic oxidation process via PMS activation to generate sulfate radicals.²¹⁵ A catalytic system, Ce–Mg/ Al_2O_3 /ozone has shown good efficiency for decomposition of resistant petroleum organic wastes.²¹⁶

Mesoporous CuO/TiO_2 nanotubes and CuO nanorods-reduced graphene oxide prepared for catalytic oxidation of air pollutant CO to CO_2 .²¹⁷ Mixed metal oxides of Fe–W–Ce²¹⁸ and V_2O_5 – WO_3/TiO_2 ,²¹⁹ used for conversion of NO_x with NH_3 into N_2 and H_2O . Oxidative dehydrogenation of ethane to ethylene and reduction of N_2O could be simultaneously performed by using $\text{Cr}/\text{Al}_2\text{O}_3$,²²⁰ as well as N_2O has been directly decomposed on $\text{Cu–Zn}/\text{ZnAl}_2\text{O}_4$ and $\text{Zn}/\gamma\text{-Al}_2\text{O}_4$.²²¹

Wang et al.²²² have prepared red mud supported Co-oxide based catalysts as significantly effective for phenol decomposition via PMS activation. The authors also have reported natural zeolites supported Co oxide catalysts for phenol degradation through oxidation and adsorption process.²²³ Sharma et al.²²⁴ have demonstrated heterogeneous Fenton or Fenton-like reactions like $\text{H}_2\text{O}_2\text{–Fe}^{3+}$ (solid)/nano-zero-valent iron/immobilized iron and electro-Fenton-pyrite for decomposition of dyes and phenols.

Wang et al.²²⁵ have prepared MnO_2 nanoparticles as α -, β - and γ - MnO_2 obtained as nanowires, nanorods, and nanofibres respectively. The prepared catalysts were tested for phenol degradation and α - MnO_2 was found to be more effective and stable in term of recyclability for phenol decomposition. They also have reported a comparative study of Mn_3O_4 , Co_3O_4 and Fe_3O_4 nanoparticles for decomposition

of phenolic contamination in aqueous solution. The catalysts are found to be effective in heterogeneous activation of PMS to produce sulfate radicals for phenol degradation and the order of catalytic activity was observed as $\text{Mn}_3\text{O}_4 > \text{Co}_3\text{O}_4 > \text{Fe}_3\text{O}_4$.²²⁶ Powder activated carbon materials have been reported as green heterogeneous metal-free catalysts for the degradation of phenol through generation of sulfate radicals.²²⁶ The degradation study shows that activated carbons were significantly effective with PMS to produce sulfate radicals compared to use with H_2O_2 and peroxydisulfate.

Galeano et al.²²⁷ have briefly introduced mixed Al/metal-pillared clays as effective catalytic system for the degradation of organic pollutants in aqueous streams. The prepared catalytic system using Fe, Cu and Mn show metal pollution prevention and an effective performance under operative conditions. Al/Fe-pillared clay has been exhibited as most active catalyst for catalytic wet peroxide oxidation (CWPO) process and possesses desirable features of a catalyst able to operate the CWPO detoxification over a wide variety of real wastewaters.²²⁷ Nair et al. have evaluated catalytic activity of Mn-substituted zinc nanoparticles ($\text{Mn}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$) prepared by sol-gel method.²²⁸ As results, catalyst found to be very active wet peroxide oxidation of *p*-chlorophenol. Zhang et al. have evaluated catalytic performance of acid-modified coal fly ash catalyst for a Fenton-like process in *p*-nitrophenol wastewater treatment.²²⁹ Zhen has briefly reviewed on cobalt oxide (Co_3O_4)²³⁰ as environmental catalysis for catalytic reduction of NO by ammonia, hydro-desulfurization of COS, ozonation degradation of phenol, photocatalytic degradation of selective hydration of aromatic nitriles,²³¹ oxidative dehydrogenation of propane,²³² oxidative dehydrogenation of cyclohexane,²³³ and hydrogen production by photo-catalytically.²³⁴ Kumar et al.²³⁵ have introduced various synthesis routes for aerogels and metal-organic framework as well as potential utilities as heterogeneous catalysts for environmental and energy applications. These include removal of heavy metals, CO_2 capture and reduction, photodegradation of pollutants, air cleanup and water splitting as environmental and energy production through hydrogen, methane reforming, CO_2 conversion and NO_x removal as energy applications.

So far we have discussed on advanced oxidation processes (Fenton process, ozonation, sonolysis etc.) to reduce/control the organic pollutants from the aqueous and air, where active radicals involve in decomposition of large polluting molecules to small harmless molecules. Besides use of such heterogeneous catalysis, photocatalysis gaining huge attention with significant advancements being made in the synthesis of novel catalytic materials and nano-structures,

and the design of efficient processes for the degradation of aqueous as well as atmospheric organic pollutants. Thus, photocatalysis is considered to be the most practical tool due to its usage of sunlight to decompose organic pollutants to convert them into valuable chemicals. A number of semiconductor-based (TiO_2 , CdS, CdSe, ZnO, SiO_2 , ZrO_2 etc.) photocatalysis are now well established and are being employed as environment-friendly catalytic process.

Many researchers are engaged to design novel photocatalyst by considering the current environmental challenges and providing a clean and sustainable photocatalytic system. Dong et al.^{236–238} have reported photocatalytic NO removal by using O/La co-functionalized amorphous graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) which shows good efficiency. The incorporation of O and La form interlayer induce electron transportation which could reduce energy barriers and hence enhanced photocatalytic activity. The authors also have reported photocatalytic activity of Sr-intercalated $\text{g-C}_3\text{N}_4$ for oxidation of NO to convert non-toxic molecules selectively for air pollution control.²³⁸ O/Ba co-functionalized amorphous carbon nitride system has exhibited enhanced photocatalytic NO removal rate with good selectivity to produces NO_2^- and NO_3^- while it also preventing the generation of toxic intermediate NO_2 . The authors also have prepared thermally and chemically stable Bi_3WO_6 tested for photocatalytic NO oxidization.²³⁹ The presence of oxygen vacancy narrows the band gap and also promotes visible light absorption hence; the enhanced activity was observed.

Particularly, CdS as a photocatalyst has gained extensive interest due to its relatively narrow band-gap for visible-light absorption and sufficiently negative potential of the conduction band edge for the reduction of protons.²⁴⁰ Generally, CdS is one of the most prominent semiconductors as a visible-light-responsive photocatalyst with a band gap of 2.4 eV among the other photocatalyst being used for hydrogen production. Cheng et al.²⁴¹ have introduced CdS and CdS-based photocatalyst that possess excellent photocatalytic activity in terms of solar-fuel generation and environmental cleaning through degradation of pollutants, hydrogen production and reduction of CO_2 to hydrocarbon fuels. The monovalent CdS nanoparticles with different crystal forms (*wurtzite* phase and *zinc blende* phase) have been evaluated for the hydrogen production.²⁴¹ Zhang et al. have prepared CdS nanorods by a one-step solvothermal method and obtained an excellent photocatalytic activity for H_2 production with a high dispersion of Pt.²⁴² There are many studies reported on binary CdS-based photocatalytic nano-composite materials such as CdS/ ZnO ,²⁴³ CdS/ TiO_2 ,^{244,245} and CdS/graphene,²⁴⁶ CdS/sulfides (CdS/CuS),²⁴⁷ CdS/ ZnS ,²⁴⁸ Bi_2S_3 /CdS^{249,250} and, CdS/ WS_2 ,²⁵¹ MoS_2 /CdS,²⁵² for

H_2 evolution. The main advantage of the combination of such nano-composite construction is to improve photochemical properties and crystal forms of CdS and also increase the photogenerated electrons for photocatalytic H_2 production. Recently, researchers have made efforts to combine CdS with other two co-catalysts to form ternary CdS-based photocatalysts such as CdS/ WS_2 /graphene,²⁵³ CdS/ MoS_2 /graphene,^{254–256} CdS/ $\text{g-C}_3\text{N}_4$ /CuS,²⁵⁷ CdS/ Ag_2S /carbon-nano-tube (CNT),²⁵⁸ CdS/ WC/TiO_2 ,²⁵⁹ and CdS/ MoS_2 / TiO_2 .²⁶⁰ The photocatalytic hydrogen production was enhanced by using these ternary CdS-based photocatalysts and also preventing photo-corrosion.

Beside use of CdS for photocatalytic H_2 production, it also makes significant contribution for environment cleaning as well as energy storage through conversion of carbon dioxide (CO_2) to produce useful hydrocarbons such as methane, methanol, formic acid and formaldehyde etc. The reduced graphene oxide/CdS nano-rods composite exhibits very good photocatalytic activity for conversion of CO_2 to methane where graphene oxide act as photoelectron acceptor and thus reduced recombination rate of photogenerated electron-hole pairs and hence enhanced photo-response.²⁶¹ CdS-based, CdS/ ZnIn_2S_4 ,²⁶² nano-composite and CdS/ TiO_2 ,²⁶³ nano-tube array has been exhibited with efficient dye degradation under visible irradiation and under sonication respectively.

TiO_2 , as an extensively studied and robust material in the field of photocatalysis research, as it was beginning from 1972 Fujishima and Honda et al., about the noble work of H_2 production from water splitting.²⁶⁴ TiO_2 nanoparticles have wide range of applications and acts as back bone for many advanced process and devices such dye sensitized solar cells, sensors and rechargeable batteries/super capacitors etc.^{265,266} Many more applications have already been well set for commercial productions like biomedical devices and drug delivery which has made TiO_2 itself undivided part of photo-induced processes. Many researchers have reviewed about possible surface and structural modification for TiO_2 and also about their catalytic mechanism reveal more interesting facts about TiO_2 photocatalysis.^{244,266–268}

Among all the possible applications of TiO_2 as photocatalyst, it has been extensively used for photodegradation of various pollutants. It is very interesting to study about TiO_2 semiconductor based photocatalytic mechanism upon absorption of photons and generation of reactive radical species through electron-hole pair recombination process. The pure mesoporous TiO_2 , TiO_2 -nanorods and -nanotubes have been demonstrated for their excellent photocatalytic activity for degradation of organic pollutants under suitable conditions.

In addition, progressive performances continuing through surface modification into TiO_2 by doping metal and non-metals which enhance visible light adsorption. Recently we have reviewed on the possible surface modification into TiO_2 photocatalysts as well as including development of Plasmonic photocatalyst.^{245b}

As part of environmental catalysts, MOFs also have been explored for air and water environmental remediation processes including removal of toxic metal ions, photocatalytic degradation of toxic dyes and other organic pollutants.²⁶⁹ Recently MOFs of MIL-125(Ti)- NH_2 , MIL-125(Ti) and MIL-125(Ti)- $(\text{NH}_2)_2$,²⁷⁰ UiO-66 and UiO-66- NH_2 ,²⁷¹ MOF-5,²⁷² NH_2 -UiO-66(Zr),²⁷³ NH_2 -UiO-66(Hf)²⁷⁴ and HKUST-1²⁷⁵ are considered to have good to excellent gas adsorption capacity.

4 Major challenges for heterogeneous catalysis

Since over the many decades, catalysis researchers have been at the lead in addressing numerous challenges in generation of efficient energy resources, controlled on pollution, and sustainable development. The advanced strategies and approaches being developed by the catalysis community have led to significant changes, contributing to economic growth.

At the core of these efforts, heterogeneous catalysis offers low cost, high conversion efficiency, and product selectivity, enabling a wide range of industrial processes to proceed effectively. The recyclability of heterogeneous catalysts promotes green and sustainable manufacturing while preventing secondary pollution. From an economic perspective, the Heterogeneous Catalyst Market was valued at USD 24.6 billion in 2023 and is expected to register a compound annual growth rate (CAGR) of over 4.8 % between 2024 and 2032.²⁷⁶ More than 80 % industries such as petrochemicals, chemicals, and refining continue to expand globally; the demand for heterogeneous catalysts is increasing.

However, applying heterogeneous catalysis on an industrial scale presents a exclusive set of challenges that can influence efficiency, cost, and sustainability. Therefore, its advancement requires the search for new materials with optimal catalytic activity and economic feasibility. In many important cases, catalyst deactivation often leads to a reduction in overall catalyst performance due to substantial or complete blocking of surface sites, carbon deposition, pore plugging, and the destruction of the catalyst. Catalyst deactivation (nonselective and selective deactivation) must

be estimated in an industrial unit using temperature profiles, which can then guide decisions regarding improved process control and timely catalyst replacement.

The efficiency of a heterogeneous catalyst is strongly dependent on the ability of reactants to reach and interact with active sites on the catalyst surface. In the context of biodiesel production, the catalyst surface should exhibit hydrophobic properties, such as mesoporous surface reactivity, which helps facilitate the adsorption of oily hydrophobic species onto the catalyst's surface. Therefore, the hydrophobicity of acid sites has become a key focus, as it minimizes poisoning by polar molecules. In case of high temperatures, catalyst may undergo structural changes leading to further loss of catalytic activity, compromising the process efficiency and leading to potential process failures. Developing and testing catalysts with sustainable thermal stability is essential for applications that involve high temperatures. Another important issue is translating a catalytic process from the laboratory to an industrial scale. Heat and mass transfer conditions are not identical at both scales, so scalability must be carefully considered for successful industrial application.

In general, variations or modifications in synthetic methods that controls the physico-chemical and thermal characteristics of heterogeneous catalysts that can lead to significant changes in reactivity and selectivity of the catalyst. Thus, we have to continue to design and modify new with the present characteristics to understand the interaction of the whole catalytic system. Additionally, understanding the effects of reaction conditions on the catalyst at a molecular level still requires the assistance of advanced, predetermined technologies. In this regard, computational screening technology can be a viable solution, providing acceptable estimations of surface reactivity with relatively low-cost information.

5 Conclusions

The present review article providing a prior literature on advancement of heterogeneous catalysis with its environmental and economic benefits in the field of energy generation and sustain the available feedstock as well. The varieties of materials have been discussed to explore their possible utilities as an emerging aspect of the materials science. Heterogeneous catalytic systems such as solid acids (H-form zeolites, sulfated-oxides, sulfonic ion exchangers, mesoporous silica materials, zirconia and titania supported materials), solid bases (β -zeolites, hydrotalcites, alkali metal- and mixed metal-oxides), transition metal based-MOFs catalysts are playing key role for biodiesel production

as an alternative fuel source. As a part of heterogeneous catalysis, photocatalysis has major contribution for the environment remediation and exhibits as a promising green approach for the future demand with further investigation.

The present report could help to rational design a novel material by tuning the surface morphology and structural properties, and hence an efficient and non-expensive catalytic system as a part of eco-friendly way out to overcome the present challenges. The further progress in the heterogeneous catalytic systems will facilitate alternative fuel production and thus they can substitute the present expensive and hazardous catalytic systems.

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References

- (a) Bartholomew, C. H.; Farrauto, R. J. *Fundamentals of Industrial Catalytic Processes*, 2nd ed.; Wiley-Interscience: NJ, 2005.
- (b) Sheldon, R. A.; Arends, I.; Henefeld, U. *Green Chemistry and Catalysis*; Wiley VCH: Weinheim, Germany, 2007.
- (c) Gates, B. C. *Catalytic Chemistry*; Wiley: NY, 1991.
- Waclawek, S.; Padil, V. V. T.; Cernik, M. Major Advances and Challenges in Heterogeneous Catalysis for Environmental Applications: A Review. *Ecol. Chem. Eng. S.* **2018**, 25 (1), 9–34.
- Sani, Y. M.; Daud, W. M. A. W.; Aziz, A. R. A. Activity of Solid Acid Catalysts for Biodiesel Production: A Critical Review. *Appl. Catal. A: Gen.* **2014**, 470, 140–161.
- Catalyst market size, share, trends, industry growth report 2019–2025; Grand View Research: San Francisco, CA, 2018. URL: <https://www.grandviewresearch.com/industry-analysis/catalyst-market/request/rs1>.
- Thomas, J. M. Summarizing Comments on the Discussion and a Prospectus for Urgent Future Action. *Phil. Trans. R. Soc. A.* **2016**, 374, 20150226.
- Chouhan, A. P. S.; Sarma, A. K. Modern Heterogeneous Catalysts for Biodiesel Production: A Comprehensive Review. *Renew. Sust. Energ. Rev.* **2011**, 15, 4378–4399.
- (a) Sa, J. *Fuel Production with Heterogeneous Catalysis*, 1st ed.; CRC Press Taylor & Francis Group: FL, **2018**. (b) Su, F.; Guo, Y. Advancements in Solid Acid Catalysts for Biodiesel Synthesis. *Green Chem.* **2014**, 16, 2934–2957. (c) Parangi, T.; Mishra, M. K. Solid Acid Catalysts for Biodiesel Production. *Comments Inorg. Chem.* **2020**, 40 (4), 176–216.
- Whang, H. S.; Lim, J.; Choi, M. S.; Lee, J.; Lee, H. Heterogeneous Catalysts for Catalytic CO₂ Conversion into Value-Added Chemicals. *BMC Chem. Eng.* **2019**, 1–9; <https://doi.org/10.1186/s42480-019-0007-7>.
- Hara, M. Biomass Conversion by a Solid Acid Catalyst. *Energ. Environ. Sci.* **2010**, 3, 601–607.
- Ignacio, M.-C. Catalytic Materials: Concepts to Understand the Pathway to Implementation. *Ind. Eng. Chem. Res.* **2021**, 60 (51), 18543–18938.
- Volker, H. Catalytic Process Development for Renewable Materials. *Green Process. Synth.* **2013**, 2 (4), 375–376.
- Moulijn, J. A.; van Santen, R. A. History of Catalysis. In *Contemporary Catalysis: Science, Technology, and Applications*; Kamer, P. C. J.; Vogt, D.; Thybaut, J., Eds. The Royal Society of Chemistry: Croydon, UK, 2017; pp 1–28.
- Zhang, J.; Chen, H.; Duan, X.; Sun, H.; Wang, S. Photothermal Catalysis: From Fundamentals to Practical Applications. *Mater. Today* **2023**, 68, 234–253.
- (a) Djaballah, M. L.; Merouani, S.; Bendjama, H.; Hamdaoui, O. Development of a Free Radical-Based Kinetics Model for the Oxidative Degradation of Chlorazol Black in Aqueous Solution Using Periodate Photoactivated Process. *J. Photochem. Photobio. A: Chem.* **2021**, 408, 113102. (b) Hamdaoui, O.; Merouani, S.; Benmahmoud, H. C.; Ait Idir, M.; Ferkous, H.; Alghyamah, A. Ultrasound/Chlorine: A Novel Synergistic Sono-Hybrid Process for Allura Red AC Degradation. *Catalysts* **2022**, 12, 1171. (c) Bekkouche, S.; Merouani, S.; Hamdaoui, O.; Bouhelassa, M. Efficient Photocatalytic Degradation of Safranin O by Integrating Solar-UV/TiO₂/persulfate Treatment: Implication of Sulfate Radical in the Oxidation Process and Effect of Various Water Matrix Components. *J. Photochem. Photobio. A: Chem.* **2017**, 345, 80–91.
- (a) Meghlaoui, F. Z.; Merouani, S.; Hamdaoui, O.; Bouhelassa, M.; Ashokkumar, M. Rapid Catalytic Degradation of Refractory Textile Dyes in Fe(II)/chlorine System at Near Neutral pH: Radical Mechanism Involving Dichlorine Radical Anion (Cl₂^{•−})-Mediated Transformation Pathways and Impact of Environmental Matrices. *Sep. Purif. Technol.* **2019**, 115685. (b) Meghlaoui, F. Z.; Merouani, S.; Hamdaoui, O.; Alghyamah, A.; Bouhelassa, M.; Ashokkumar, M. Fe(III)-catalyzed Degradation of Persistent Textile Dyes by Chlorine at Slightly Acidic Conditions: the Crucial Role of Cl₂^{•−} Radical in the Degradation Process and Impacts of Mineral and Organic Competitors. *Asia Pac. J. Chem. Eng.* **2020**, 16 (1), 2553. (c) Merouani, S.; Dehane, A.; Belghit, A.; Hamdaoui, O.; Tobba, Y. A.; Lahlou, C.; Shah, M. P. Protonated Hydroxylamine-Assisted Iron Catalytic Activation of Persulfate for the Rapid Removal of Persistent Organics from Wastewater. *Clean – Soil, Air, Water* **2022**, 51 (3), 2100304.
- Bekkouche, S.; Bouhelassa, M.; Aissa, A. K.; Baup, S.; Gondrexon, N.; Petrier, C.; Merouani, S.; Hamdaoui, O. Synergy between Solar Photocatalysis and High Frequency Sonolysis toward the Degradation of Organic Pollutants in Aqueous Phase – Case of Phenol. *Desalin. Water Treat.* **2017**, 62, 457–464.
- Bouchareb, M. K.; Berkani, M.; Merouania, S.; Bouhelassa, M. Box-Wilson Design Modeling of Photocatalytic Degradation of Industrial Dye and Wastewater in Semi-pilot Solar Photoreactor. *Water Sci. Technol.* **2020**, 82 (7), 1393–1403.
- (a) Xu, Z.; Li, Y.; Shi, H.; Lin, Y.; Wang, Y.; Wang, Q.; Zhu, T. Application Prospect of K Used for Catalytic Removal of NO_x, CO_x, and VOCs from Industrial Flue Gas: A Review. *Catalysts* **2021**, 11 (4), 419. (b) Zhao, H.; Meng, P.; Gao, S.; Wang, Y.; Sun, P.; Wu, Z. Recent Advances in Simultaneous Removal of NO_x and VOCs over Bifunctional Catalysts via SCR and Oxidation Reaction. *Sci. Total Environ.* **2024**, 906.
- (a) Dhal, G. C.; Dey, S. Catalytic Conversion of Carbon Monoxide into Carbon Dioxide over Spinel Catalysts: An Overview. *Mater. Sci. Energy*

- Technol.* **2019**, 2 (3), 575–588.(b) Kembo, J. P. N.; Wang, J.; Luo, N.; Gao, F.; Yi, H.; Zhao, S.; Zhou, Y.; Tang, X. A Review of Catalytic Oxidation of Carbon Monoxide over Different Catalysts with an Emphasis on Hopcalite Catalysts. *New J. Chem.* **2023**, 47, 20222–20247.
20. (a) Khouw, C. B.; Darrt, C. B.; Labinger, J. A.; Davis, M. E. Studies on the Catalytic-Oxidation of Alkanes and Alkenes by Titanium Silicates. *J. Catal.* **1994**, 149 (1), 195–205.(b) Fabrice, D.; Jacques, B. Jr.; Daniel, D.; Isabelle, G.; Gil, M. Catalytic Oxidation of Heavy Hydrocarbons over Pt/Al₂O₃. Influence of the Structure of the Molecule on its Reactivity. *Appl. Catal. B Environ.* **2010**, 95 (3–4), 217–227.
 21. Wang, L.; Zhang, X.; Yang, L.; Wang, C.; Wang, H. Photocatalytic Reduction of CO₂ Coupled with Selective Alcohol Oxidation under Ambient Conditions. *Catal. Sci. Technol.* **2015**, 5, 4800–4805.
 22. Laverdura, U. P.; Rossi, L.; Ferella, F.; Courson, C.; Zarli, A.; Alhajjoussef, R.; Gallucci, K. Selective Catalytic Hydrogenation of Vegetable Oils on Lindlar Catalyst. *ACS Omega* **2020**, 5 (36), 22901–22913.
 23. Jing, Z.; Guo, Y.; Wang, Q.; Yan, X.; Yue, G.; Li, Z.; Liu, H.; Qin, R.; Zhong, C.; Li, M.; Xu, D.; Yao, X.; Shuai, X.; Shuai, M. Ambient Hydrogenation of Solid Aromatics Enabled by a High Entropy Alloy Nanocatalyst. *Nat. Commun.* **2024**, 15, 5806–5816.
 24. (a) Ashida, Y.; Mizushima, T.; Arashiba, K.; Egi, A.; Tanaka, H.; Yoshizawa, K.; Nishibayashi, Y. Catalytic Production of Ammonia from Dinitrogen Employing Molybdenum Complexes Bearing N-Heterocyclic Carbene-Based PCP-type Pincer Ligands. *Nat. Synth.* **2023**, 2, 635–644.(b) Hattori, M.; Iijima, S.; Nakao, T.; Hosono, H.; Hara, M. Solid Solution for Catalytic Ammonia Synthesis from Nitrogen and Hydrogen Gases at 50 °C. *Nat. Commun.* **2020**, 11, 2001.
 25. (a) Liu, X.-M.; Lu, G. Q.; Yan, Z.-F.; Beltramini, J. Recent Advances in Catalysts for Methanol Synthesis via Hydrogenation of CO and CO₂. *Ind. Eng. Chem. Res.* **2003**, 42 (25), 6518–6530.(b) Salami, R.; Zeng, Y.; Han, X.; Rohani, S.; Zheng, Y. Exploring Catalyst Developments in Heterogeneous CO₂ Hydrogenation to Methanol and Ethanol: A Journey through Reaction Pathways. *J. Energy Chem.* **2025**, 101, 345–384.
 26. Choi, Y.; Wu, X.; Lee, J.-W.; Na, K. Catalytic Dehydrogenation for Hydrogen Production Controlled by Metal-Supported Heterogeneous Catalysts. *Catal. Sci. Technol.* **2024**, 14, 5784–5810.
 27. (a) Meng, H.; Yang, Y.; Shen, T.; Yin, Z.; Zhang, J.; Yan, H.; Wei, M. Highly Efficient Hydrogen Production from Dehydrogenation Reaction of Nitrogen Heterocycles via Pd⁰–Pd^{δ+} Synergistic Catalysis. *ACS Catal.* **2023**, 13 (13), 9234–9244.(b) Chulliyil, H. M.; Hamdani, I. R.; Ahmad, A.; Pillantakath, A. R.; Shoaibi, A. A.; Srinivasakannan, C.; Hossain, M. M. Catalytic Dehydrogenation of Methane to Hydrogen and Carbon Nanostructures with Fe–Mo Bimetallic Catalysts. *Ind. Eng. Chem. Res.* **2024**, 63 (9), 3853–3866.(c) Voskresenskaya, E. N.; Kirilets, V. M.; Taran, O. P.; Kuznetsov, B. N. Hydrogen Production by the Heterogeneous Catalytic Dehydrogenation of Formic Acid: A Review. *Catal. Ind.* **2024**, 16, 339–349.
 28. Wittich, K.; Kramer, M.; Bottke, N.; Schunk, S. A. Catalytic Dry Reforming of Methane: Insights from Model Systems. *Chem. Cat. Chem.* **2020**, 12 (8), 2130–2147.
 29. Frontera, P.; Antonucci, P. L.; Macario, A. Focus on Materials for Sulfur-Resistant Catalysts in the Reforming of Biofuels. *Catalysts* **2021**, 11 (9), 1029.
 30. Li, D.; Li, X.; Gong, J. Catalytic Reforming of Oxygenates: State of the Art and Future Prospects. *Chem. Rev.* **2016**, 116 (19), 11529–11653.
 31. Aouad, S.; Labaki, M.; Ojala, S.; Seelam, P.; Turpeinen, E.; Gennequin, C.; Estephane, J.; Abi-Aad, E. A Review on the Dry Reforming Processes for Hydrogen Production: Catalytic Materials and Technologies. In *Frontiers in Ceramic Science Catalytic Materials for Hydrogen Production and Electro-oxidation Reactions*; Cesario, M. R.; Gennequin, C.; Abi-Aad, E.; De Macedo, D. A., Eds; Bentham Science Publisher: Portugal, Vol. 2, 2018.
 32. Thangaraj, B.; Solomon, R. P.; Muniyandi, B.; Ranganathan, S.; Lin, L. Catalysis in Biodiesel Production- A Review. *Clean Energ.* **2019**, 3 (1), 2–23.
 33. (a) Lee, A. F.; Bennett, J. A.; Manayil, J. C.; Wilson, K. Heterogeneous Catalysis for Sustainable Biodiesel Production via Esterification and Transesterification. *Chem. Soc. Rev.* **2014**, 43, 7887–7916.(b) Marwaha, A.; Dhir, A.; Mahla, S. K.; Mohapatra, S. K. An Overview of Solid Base Heterogeneous Catalysts for Biodiesel Production. *Catal. Rev.* **2018**, 60, 594–628.
 34. Kiss, A. A.; Dimian, A. C.; Rothenberg, G. Solid Acid Catalysts for Biodiesel Production -Towards Sustainable Energy. *Adv. Synth. Catal.* **2006**, 348, 75–81.
 35. Helwani, Z.; Othman, M. R.; Aziz, N.; Fernando, W. J. N.; Kim, J. Technologies for Production of Biodiesel Focusing on Green Catalytic Techniques: A Review. *Fuel Process. Technol.* **2009**, 90, 1502–1514.
 36. Sharma, Y. C.; Singh, B. Development of Biodiesel: Current Scenario. *Renew. Sustain. Energy Rev.* **2009**, 13, 1646–1651.
 37. Okoronkwo, M. U.; Galadima, A.; Leke, L. Advances in Biodiesel Synthesis: From Past to Present. *Elixir Appl. Chem.* **2012**, 43, 6924–6945.
 38. West, A. H.; Posarac, D.; Ellis, N. Assessment of Four Biodiesel Production Processes Using HYSYS. *Plant. Bioresour Technol* **2008**, 99, 6587–6601.
 39. Lourinho, G.; Brito, P. Advanced Biodiesel Production Technologies: Novel Developments. *Rev. Environ. Sci. Biotechnol.* **2014**, 14 (2), 287–316.
 40. Miao, S.; Shanks, B. H. Esterification of Biomass Pyrolysis Model Acids over Sulfonic Acid-Functionalized Mesoporous Silicas. *Appl. Catal. A: Gen.* **2009**, 359 (1–2), 113–120.
 41. Puna, J. F.; Gomes, J. F.; Correia, M. J.; Soares Dias, A. P.; Bordado, J. C. Advances on the Development of Novel Heterogeneous Catalysts for Transesterification of Triglycerides in Biodiesel. *Fuel* **2010**, 89, 3602–3606.
 42. Zhang, Z. Branched Biodiesels. US 0045731 A1, 2008.
 43. Pozzo, D. M. D.; dos Santos, J. A. A.; Junior, E. S.; Santos, R. F.; Feiden, A.; de Souza, S. N. M.; Burgardt, I. Free Fatty Acids Esterification Catalyzed by Acid Faujasite Type Zeolite. *RSC Adv.* **2019**, 9, 4900–4907.
 44. Septiani, U.; Putri, R. A.; Jamarun, N. Synthesis of Zeolite ZSM-5 from Rice Husk Ash as Catalyst in Vegetable Oil Transesterification for Biodiesel Production. *Der Pharm. Lett.* **2016**, 8 (19), 86–91.
 45. Park, Y. M.; Lee, D. W.; Kim, D. K.; Lee, J. S.; Lee, K. Y. The Heterogeneous Catalyst System for the Continuous Conversion of Free Fatty Acids in Used Vegetable Oils for the Production of Biodiesel. *Catal. Today* **2008**, 131, 238–243.
 46. Brito, A.; Borges, M.; Garin, M.; Hernandez, A. Biodiesel Production from Waste Oil Using Mg–Al Layered Double Hydroxide Catalysts. *Energy. Fuel.* **2009**, 23, 2952–2958.
 47. Doyle, A. M.; Alismaeel, Z. T.; Albayati, T. M.; Abbas, A. S. High Purity FAU-type Zeolite Catalysts from Shale Rock for Biodiesel Production. *Fuel* **2017**, 199, 394–402.
 48. Noor Al-Jammal Zayed Al-Hamamre Mohammad Alnaief Manufacturing of Zeolite Based Catalyst from Zeolite Tuft for Biodiesel Production from Waste Sunflower Oil. *Renew. Energy.* **2016**, 93, 449–459.

49. Fereidooni, L.; Tahvildari, K.; Abdollah, A.; Sharif, M. Biodiesel Production from Methanolysis of Refined Vegetable Oil through KOH/zeolite Catalyst. *Der Pharma Chem. J* **2017**, 4 (4), 85–90.
50. Brito, A.; Borges, M. E.; Otero, N. Zeolite Y as a Heterogeneous Catalyst in Biodiesel Fuel Production from Used Vegetable Oil. *Energ. Fuel*. **2007**, 21, 3280–3283.
51. Carrero, A.; Vicente, G.; Rodríguez, R.; Linares, M.; del Peso, G. L. Hierarchical Zeolites as Catalysts for Biodiesel Production from Nannochloropsis Microalga Oil. *Catal. Today* **2011**, 167, 148–153.
52. Wang, Y.-Y.; Lee, D. J.; Chen, B.-H. Low-Al Zeolite Beta as a Heterogeneous Catalyst in Biodiesel Production from Microwave-Assisted Transesterification of Triglycerides. *Energy Proc.* **2014**, 61, 918–921.
53. Dang, T.-H.; Chen, B.-H.; Lee, D.-J. Optimization of Biodiesel Production from Transesterification of Triolein Using Zeolite LTA Catalysts Synthesized from Kaolin Clay. *J. Taiwan Inst. Chem. Eng.* **2017**, 79, 14–22.
54. Dianursanti, D.; Hayati, S. J.; Putri, D. N. Biodiesel Synthesis via Transesterification of Lipid Chlorophyta Cultivated in Walne Rich Carbon Medium Using KOH/Zeolite Catalyst. *AIP Conf. Proc.* **2017**, 1904, 020065.
55. Hartono, R.; Wijanarko, A.; Hermansyah, H. Synthesis of Biodiesel Using Local Natural Zeolite as Heterogeneous Anion Exchange Catalyst. *IOP Conf. Ser. Mater. Sci. Eng.* **2018**, 345; <https://doi.org/10.1088/1757-899x/345/1/012002>.
56. Hassani, M.; Najafpour, G. D.; Mohammadi, M.; Rabiee, M. Preparation, Characterization and Application of Zeolite Based Catalyst for Production of Biodiesel from Waste Cooking Oil. *J. Sci. Ind. Res.* **2014**, 73, 129–133.
57. Hidayat, A.; Mukti, M. I. F.; Handoko, B.; Sutrisno, B. Biodiesel Production from Rice Bran Oil over Modified Natural Zeolite Catalyst. *Int. J. Technol.* **2018**, 2, 400–411.
58. Hidayat, A.; Sutrisno, B. Free Fatty Acids Esterification on Palm Oil Sludge Using Zirconia-Supported Indonesian Natural Zeolite as Heterogeneous Catalyst. *Orient. J. Chem.* **2018**, 34 (5), 2464–2470. Mukti
59. Intarapong, P.; Luengnaruemitchai, A.; Jai-In, S. Transesterification of Palm Oil over KOH/NaY Zeolite in a Packed-Bed Reactor. *Int. J. Renew. Energ. Res* **2011**, 1 (4), 271–280.
60. Noiroj, K.; Intarapong, P.; Luengnaruemitchai, A.; JaiIn, S. A Comparative Study of KOH/Al₂O₃ and KOH/NaY Catalysts for Biodiesel Production via Transesterification from Palmoil. *Renew. Energy* **2009**, 34, 1145–1150.
61. Luz Martinez, S.; Romero, R.; Lopez, J. C.; Romero, A.; Sanchez Mendieta, V.; Natividad, R. Preparation and Characterization of CaO nanoparticles/NaX Zeolite Catalysts for the Transesterification of Sunflower Oil. *Ind. Eng. Chem. Res.* **2011**, 50 (5), 2665–2670.
62. Mowla, D.; Rasti, N.; Keshavarz, P. Transesterification of Waste Cooking Oil for Biodiesel Production Using Modified Clinoptilolite Zeolite as a Heterogeneous Catalyst. *Int. J. Chem. Mol. Eng.* **2016**, 10 (9), 1201–1205.
63. Setianingsih, A.; Wisrayetti, K.; Bahri, S. Effect of Lanthanum-Natural Zeolite, La/NZA Catalyst on Biodiesel Production from Crude Palm Oil. *IOP Conf. Ser. Mater. Sci. Eng.* **2018**, 345, 012007.
64. Singh, D.; Ganesh, A.; Mahajani, S. Heterogeneous Catalysis for Biodiesel Synthesis and Valorization of Glycerol. *Clean Techn. Environ. Policy*. **2015**, 17 (4), 1103–1110.
65. Volli, V.; Purkait, M. K. Selective Preparation of Zeolite X and A from Flyash and its Use as Catalyst for Biodiesel Production. *J. Hazard Mater.* **2015**, 297, 101–111.
66. Wang, Y.-Y.; Wang, H.-H.; Chuang, T.-L.; Chen, B.-H.; Lee, D.-J. Biodiesel Produced from Catalyzed Transesterification of Triglycerides Using Ion-Exchanged Zeolite Beta and MCM-22. *Energy Proc.* **2014**, 61, 933–936.
67. Xue, W.; Zhou, Y.-C.; Song, B.-A.; Shi, X.; Wang, J.; Yin, S.-T.; Jin, L.-H.; Yang, S. Synthesis of Biodiesel from *Jatropha Curcas* L. Seed Oil Using Artificial Zeolites Loaded with CH₃COOK as a Heterogeneous Catalyst. *Nat. Sci.* **2009**, 1, 55–62.
68. Vieira, S. S.; Magriotis, Z. M.; Santos, N. A. V.; Saczk, A. A.; Hori, C. E.; Arroyo, P. A. Biodiesel Production by Free Fatty Acid Esterification Using Lanthanum (La³⁺) and HZSM-5 Based Catalysts. *Bioresour. Technol.* **2013**, 133, 248–255.
69. Prinsen, P.; Luque, R.; Gonzalez-Arellano, C. Zeolite Catalyzed Palmitic Acid Esterification. *Micropor. Mesopor. Mater.* **2018**, 262, 133–139.
70. Chang, F.; Zhou, Q.; Pan, H.; Liu, X.-F.; Zhang, H.; Yang, S. Solid Mixed-Metal-Oxide Catalysts for Biodiesel Production: A Review. *Energy Technol.* **2014**, 2, 865–873.
71. Vedrine, J. C. Heterogeneous Catalysis on Metal Oxides. *Catalysts* **2017**, 7, 341.
72. da Conceicao, L. R. V.; Carneiro, L. M.; Rivaldi, J. D.; de Castro, H. F. Solid Acid as Catalyst for Biodiesel Production via Simultaneous Esterification and Transesterification of Macaw Palm Oil. *Ind. Crops Prod.* **2016**, 89, 416–424.
73. Anggoro, I. D. D.; Buchori, L.; Rahmawati, D. A.; Intaningrum, D. Active Acid Catalyst of Sulphated Zinc Oxide for Transesterification of Soybean Oil with Methanol to Biodiesel. *Proc. Environ. Sci.* **2015**, 23, 385–393.
74. Peters, T. A.; Benes, N. E.; Holmen, A.; Keurentjes, J. T. F. Comparison of Commercial Solid Acid Catalysts for the Esterification of Acetic Acid with Butanol. *Appl. Catal. A* **2006**, 297, 182–188.
75. Park, J. Y.; Wang, Z. M.; Kim, D. K.; Lee, J. S. Effects of Water on the Esterification of Free Fatty Acids by Acid Catalyst. *Renew. Energy* **2010**, 35 (3), 614–618.
76. Liu, Y. J.; Lotero, E.; Goodwin, J. G. A Comparison of the Esterification of Acetic Acid with Methanol Using Heterogeneous versus Homogeneous Acid Catalysis. *J. Catal.* **2006**, 242, 278–286.
77. Liu, Y. J.; Lotero, E.; Goodwin, J. G. Effect of Carbon Chain Length on Esterification of Carboxylic Acids with Methanol Using Acid Catalysis. *J. Catal.* **2006**, 243, 221–228.
78. Guerreiro, L.; Castanheiro, J. E.; Fonseca, I. M.; Aranda, R. M. M.; Ramos, A. M.; Vital, J. Transesterification of Soybean Oil over Sulfonic Acid Functionalized Polymeric Membranes. *Catal. Today* **2006**, 118, 166–171.
79. Lopez, D. E.; Goodwin, J. D. Jr.; Bruce, D. A.; Lotero, E. Transesterification of Triacetin with Methanol on Solid Acid and Base Catalysts. *Appl. Catal. A* **2005**, 295, 97–105.
80. Lopez, D. E.; Goodwin, J. D. Jr.; Bruce, D. A. Transesterification of Triacetin with Methanol on Nafion® Acid Resins. *J. Catal.* **2007**, 245, 381–391.
81. Russbueltdt, B. M. E.; Hoelderich, W. F. New Sulfonic Acid Ion-Exchange Resins for the Preesterification of Different Oils and Fats with High Content of Free Fatty Acids. *Appl. Catal. A* **2009**, 362, 47–57.
82. Barros, S. D. T.; Coelho, A. V.; Lachter, E. R.; San Gil, R. A. S.; Dahmouche, K.; Pais da Silva, M. I.; Souza, A. L. F. Esterification of Lauric Acid with Butanol over Mesoporous Materials. *Renew. Energy*. **2013**, 50, 585–589.
83. Serio, M. D.; Tesser, R.; Casale, L.; Dapos, A.; Trifuoggi, M.; Santacesaria, E. Heterogeneous Catalysis in Biodiesel Production: The Influence of Leaching. *Top. Catal.* **2010**, 53, 811–819. Angelo

84. Xie, W.; Yang, Z.; Chun, H. Catalytic Properties of Lithium-Doped ZnO Catalysts Used for Biodiesel Preparations. *Ind. Eng. Chem. Res.* **2007**, *46*, 7942–7949.
85. Xie, W.; Zhao, L. Heterogeneous CaO-MoO₃ SBA-15 Catalysts for Biodiesel Production from Soybean Oil. *Energ. Convers. Manage.* **2014**, *79*, 34–42.
86. Anuradha, S.; Antony, K. J. R.; Vijayaraghavan, V. R.; Viswanathan, B. Sulfated Fe₂O₃-TiO₂ Catalyzed Transesterification of Soybean Oil to Biodiesel. *Ind. J. Chem. A.* **2014**, *53*, 1493–1499.
87. de Abreu, W. C.; de Moura, C. V. R.; Costa, J. C. S.; de Moura, E. M. Strontium and Nickel Heterogeneous Catalysts for Biodiesel Production from Macaw Oil. *J. Braz. Chem. Soc.* **2017**, *28* (2), 319–327.
88. Ong, H. R.; Khan, M. R.; Chowdhury, M. N. K.; Yousuf, A.; Cheng, C. K. Synthesis and Characterization of CuO/C Catalyst for the Esterification of Free Fatty Acid in Rubber Seed Oil. *Fuel* **2014**, *120*, 195–201.
89. Zhang, H.; Luo, X.; Shi, K.; Wu, T.; He, F.; Zhou, S.; Chen, G.; Peng, C. Highly Efficient Sulfonic/carboxylic Dual-Acid Synergistic Catalysis for Esterification Enabled by Sulfur-Rich Graphene Oxide (GO-S). *ChemSusChem* **2017**, *10* (17), 3352–3357.
90. Anisuzzaman, S. M.; Krishnaiah, D.; Bono, A.; Abang, S.; Sundang, M.; Suali, E.; Lahin, F. A.; Alawodeen, A. S. Synthesis and Characterization of Metal Oxide Promoted Alumina Catalyst for Biofuel Production. *IOP Conf. Ser. Earth Environ. Sci.* **2016**, *36*; <https://doi.org/10.1088/1755-1315/36/1/012039>.
91. Mohadesi, M.; Hojabri, Z.; Moradi, G. Biodiesel Production Using Alkali Earth Metal Oxides Catalysts Synthesized by Sol-Gel Method. *Biofuel Res. J.* **2014**, *1*, 30–33.
92. Ismail, S.; Ahmed, A. S.; Anr, R.; Hamdan, S. Biodiesel Production from castor Oil by Using Calcium Oxide Derived from Mud Clam Shell. *J. Renew. Energ.* **2016**, *2016* (1), 5274917.
93. Thitsartarn, W.; Maneerung, T.; Kawi, S. Highly Active and Durable Ca-Doped Ce-SBA-15 Catalyst for Biodiesel Production. *Energy* **2015**, *89*, 946–956.
94. Ali, S. D.; Javed, I. N.; Rana, U. L.; Nazar, M. F.; Ahmed, W.; Junaid, A.; Pasha, M.; Nazir, R.; Nazir, R. Novel SrO-CaO Mixed Metal Oxides Catalyst for Ultrasonic-Assisted Transesterification of *Jatropha* Oil into Biodiesel. *Aust. J. Chem.* **2017**, *70* (3), 258.
95. Lee, H. V.; Juan, J. C.; Taufiq-Yap, Y. H. Preparation and Application of Binary Acid-Base CaO-La₂O₃ Catalyst for Biodiesel Production. *Renew. Energy* **2015**, *74*, 124–132.
96. Wang, A.; Li, H.; Zhang, H.; Pan, H.; Yang, S. Efficient Catalytic Production of Biodiesel with Acid-Base Bifunctional Rod-like Ca-B Oxides by the Sol-Gel Approach. *Materials* **2019**, *12*, 83.
97. Lee, H. V.; Juan, J. C.; Hin, T.-Y.; Ong, H. C. Environment-friendly Heterogeneous Alkaline-Based Mixed Metal Oxide Catalysts for Biodiesel Production. *Energies* **2016**, *9*, 611.
98. Yigezu, Z. D.; Muthukumar, K. Catalytic Cracking of Vegetable Oil with Metal Oxides for Biofuels Production. *Energ. Convers. Manage.* **2014**, *84*, 326–333.
99. Refaat, A. A. Biodiesel Production Using Solid Metal Oxide Catalysts. *Int. J. Environ. Sci. Tech.* **2011**, *8* (1), 203–221.
100. Jose da Silva, M.; Cardoso, A. L. Heterogeneous Tin Catalysts Applied to the Esterification and Transesterification Reactions. *J. Catal.* **2013**, *305*, 510509.
101. Diamantopoulos, N.; Panagiotaras, D.; Nikolopoulos, D. Comprehensive Review on the Biodiesel Production Using Solid Acid Heterogeneous Catalysts. *J. Thermodyn. Catal.* **2015**, *6*, 143.
102. Du, L.; Ding, S.; Li, Z.; Lv, E.; Lu, J.; Ding, J. Transesterification of castor Oil to Biodiesel Using NaY Zeolite-Supported La₂O₃ Catalysts. *Energ. Convers. Manage.* **2018**, *173*, 728–734.
103. Salamatinia, B. Alkaline Earth Metal Oxide Catalysts for Biodiesel Production from Palm Oil: Elucidation of Process Behaviors and Modeling Using Response Surface Methodology. *Iran. J. Chem. Chem. Eng.* **2013**, *32* (1), 113–126.
104. Kiss, A. A.; Dimian, A. C.; Rothenberg, G. Biodiesel by Catalytic Reactive Distillation Powered by Metal Oxides. *Energ. Fuel* **2008**, *22*, 598–604.
105. Singh, D.; Bhoi, R.; Ganesh, A.; Mahajani, S. Synthesis of Biodiesel from Vegetable Oil Using Supported Metal Oxide Catalysts. *Energ. Fuel* **2014**, *28*, 2743–2753.
106. Newman, S.; Jones, W. Synthesis, Characterization and Applications of Layered Double Hydroxides Containing Organic Guests. *New J. Chem.* **1998**, *22*, 105–115.
107. Gomes, J. F. P.; Puna, J. F. B.; Goncalves, L. M.; Bordado, J. C. M. Study on the Use of MgAl Hydrotalcites as Solid Heterogeneous Catalysts for Biodiesel Production. *Energy* **2011**, *36*, 6770–6778.
108. Simonetti, E. A. N.; Thim, G. P.; Cortez, G. G. Ca-Al Hydrotalcites as Catalysts for Methanolysis and Ethanolysis of Soybean Oil. *Mod. Res. Catal.* **2014**, *3*, 117–127.
109. Baskaran, T.; Christopher, J.; Sakthivel, A. Progress on Layered Hydrotalcite (HT) Materials as Potential Support and Catalytic Materials. *RSC Adv.* **2015**, *5*, 98853–98875.
110. Xie, W.; Peng, H.; Chen, L. Calcined Mg-Al Hydrotalcites as Solid Base Catalysts for Methanolysis of Soybean Oil. *J. Mol. Catal. A: Chem.* **2006**, *246*, 24–32.
111. Yagiz, F.; Kazan, D.; Akin, A. N. Biodiesel Production from Waste Oils by Using Lipase Immobilized on Hydrotalcite and Zeolites. *Chem. Eng. J.* **2007**, *134*, 262–267.
112. Obadiah, A.; Kannan, R.; Ramasubbu, A.; Kumar, S. V. Mg-Al Hydrotalcites as Solid Base Catalysts for Biodiesel Production from Pongamia Oil. *J. Sci. Ind. Res.* **2012**, *71*, 131–137.
113. Martins, M. I.; Pires, R. F.; Alves, M. J.; Hori, C. E.; Reis, M. H. M.; Cardoso, V. L. Transesterification of Soybean Oil for Biodiesel Production Using Hydrotalcite as Basic Catalyst. *Chem. Eng. Trans.* **2013**, *32*, 817–822.
114. Chelladurai, K.; Rajamanickam, M. Environmentally Benign Neem Biodiesel Synthesis Using Nano-Zn-Mg-Al Hydrotalcite as Solid Base Catalysts. *J. Catal.* **2014**, *326*, 575.
115. Dierio, M. D.; Mallardo, S.; Carotenuto, G.; Tesser, R.; Santacesaria, E. Mg/Al Hydrotalcite Catalyst for Biodiesel Production in Continuous Packed Bed Reactors. *Catal. Today* **2012**, *195*, 54–58.
116. Costarrosa, L.; Leiva-Candia, D. E.; Cubero-Atienza, A. J.; Ruiz, J. J.; Dorado, M. P. Optimization of the Transesterification of Waste Cooking Oil with Mg-Al Hydrotalcite Using Response Surface Methodology. *Energies* **2018**, *11*, 302.
117. Faiz, K.; Shuhaib, E.; Unni, N.; Simon, N.; Nagapadma, M.; Gopinath, N. Synthesis of Biodiesel Using Solid Heterogeneous Catalyst Mg-Al Hydrotalcite by Transesterification from Waste Cooking Oil. *Asian J. Appl. Sci. Technol.* **2018**, *2* (2), 1013–1020.
118. Gao, L.; Teng, G.; Lv, J.; Xiao, G. Biodiesel Synthesis Catalyzed by the KF/Ca-Mg-Al Hydrotalcite Base Catalyst. *Energ. Fuel* **2010**, *24*, 646–651.
119. Gomes, J. F. P.; Puna, J. F. B.; Goncalves, L. M.; Bordado, J. C. M. Study on the Use of MgAl Hydrotalcites as Solid Heterogeneous Catalysts for Biodiesel Production. *Energy* **2011**, *36*, 6770–6778.
120. Rahul, R.; Satyarthi, J. K.; Srinivas, D. Lanthanum and Zinc Incorporated Hydrotalcites as Solid Base Catalysts for Biodiesel and Biolubricants Production. *Indian J. Chem.* **2011**, *50*, 1117–1125.
121. Ilgen, O.; Incer, I. D.; Yildiz, M.; Alptekin, E.; Boz, N.; Canakci, M.; Akin, A. N. Investigation of Biodiesel Production from Canola Oil Using Mg-Al Hydrotalcite Catalysts. *Turk. J. Chem.* **2007**, *31*, 509–514.

122. Reyero, I.; Arzamendi, G.; Gandia, L. M. Hydrotalcites as Catalysts and Catalysts Precursors for the Synthesis of Biodiesel. *Key Eng. Mater.* **2013**, 571, 1–26.
123. Teng, G.; Gao, L.; Xiao, G.; Liu, H.; Lv, J. Biodiesel Preparation from *Jatropha Curcas* Oil Catalyzed. *Appl. Biochem. Biotechnol.* **2010**, 162, 1725–1736.
124. Wang, Y.-T.; Fang, Z.; Zhang, F.; Xue, B. J. One-step Production of Biodiesel from Oils with High Acid Value by Activated Mg-Al Hydrotalcite Nanoparticles. *Bioresour. Technol.* **2015**, 93, 84–89.
125. (a) Bhayana, S.; Nandal, R.; Khatri, S. Metal Organic Frameworks as Energy Storage Material: Their Contributions and Challenges. In *Materials for Boosting Energy Storage. Vol. 1: Advances in Sustainable Energy Technologies*; Kumar, S. S.; Sharma, P.; Kumar T.; Kumar, V. Eds.; ACS Publication, USA, Vol. 1477, Ch. 6, **2024**; p. 125–144. (b) Sandhu, Z. A.; Raza, M. A.; Awwad, N. S.; Ibrahim, H. A.; Farwa, U.; Ashraf, S.; Dildar, A.; Fatima, E.; Ashraf, S.; Ali, F. Metal-organic Frameworks for Next-Generation Energy Storage Devices; a Systematic Review. *Mater. Adv.* **2024**, 5, 30–50. (c) Pettinari, C.; Tombesi, A. MOFs for Electrochemical Energy Conversion and Storage. *Inorganics* **2023**, 11, 65. (d) Silva, P.; Vilela, S. M. F.; Tome, J. P. C.; Almeida, P. F. A. Multifunctional Metal-Organic Frameworks: from Academia to Industrial Applications. *Chem. Soc. Rev.* **2015**, 44, 6774–6803.
126. (a) Nguyen, V. G.; Sharma, P.; Dzida, M.; Hung, B. V.; Le, H. S.; El-Shafay, A. S.; Le, H. C.; Le, D. T. N.; Tran, V. D. A Review on Metal-Organic Framework as a Promising Catalyst for Biodiesel Production. *Energy Fuel* **2024**, 38 (4). (b) Taddeo, F.; Vitiello, R.; Russo, V.; Tesser, R.; Turco, R.; Di Serio, M. Biodiesel Production from Waste Oil Catalysed by Metal-Organic Framework (MOF-5): Insights on Activity and Mechanism. *Catalysts* **2023**, 13, 503. (c) Basumatary, S. F.; Patir, K.; Das, B.; Saikia, P.; Brahma, S.; Basumatary, B.; Nath, B.; Basumatary, B.; Basumatary, S. Production of Renewable Biodiesel Using Metal Organic Frameworks Based Materials as Efficient Heterogeneous Catalysts. *J. Clean. Prod.* **2022**, 358. (d) Cong, W.-J.; Nanda, S.; Li, H.; Fang, Z.; Dalai, A. K.; Kozinskid, J. A. Metal-organic Framework-Based Functional Catalytic Materials for Biodiesel Production: a Review. *Green Chem.* **2021**, 23, 2595–2618. (e) Zhang, Q.; Wang, J.; Zhang, S.; Ma, J.; Cheng, J.; Zhang, Y. Zr-Based Metal-Organic Frameworks for Green Biodiesel Synthesis: A Minireview. *Bioeng (Basel)* **2022**, 9 (11), 700. (f) Gouda, S. P.; Dhakshinamoorthy, A.; Rokhum, S. L. Metal-organic Framework as a Heterogeneous Catalyst for Biodiesel Production: A Review. *Chem. Eng. J. Adv.* **2022**, 12.
127. Ghorbani-Choghamarani, A.; Taherinia, Z.; Tyula, Y. A. Efficient Biodiesel Production from Oleic and Palmitic Acid Using a Novel Molybdenum Metal-Organic Framework as Efficient and Reusable Catalyst. *Sci. Rep.* **2022**, 12, 10338.
128. Jafari, A.; Ghorbani-Choghamarani, A.; Aghavandi, A. Simple Synthesis of Novel Cr-EDTA-MOF: A Green, Reusable, and Versatile Catalyst for the Production of Biodiesel Fuel from Oleic Acid and Palmitic Acid. *ACS Omega* **2024**, 9 (5), 5255–5264.
129. Berghuis, N. T.; Jaby, F. H.; Muttaqin, M. Potential of Copper-Based MOFs as Heterogeneous Catalysts in Biodiesel Production from Waste Cooking Oil (WCO). *Resilience, EAI* **2024**; <https://doi.org/10.4108/eai.24-11-2023.2346497>.
130. Lubitz, W.; Tumas, W. Hydrogen: An Overview. *Chem. Rev.* **2007**, 107, 3900–3903.
131. Seh, Z. W.; Kibsgaard, J.; Dickens, C. F.; Chorkendorff, I.; Norskov, J. K.; Jaramillo, T. F. Combining Theory and Experiment in Electrocatalysis: Insights into Materials Design. *Sci.* **2017**, 355, <https://doi.org/10.1126/science.aad4998>.
132. Santo, V. D.; Gallo, A.; Naldoni, A.; Guidotti, M.; Psaro, R. Bimetallic Heterogeneous Catalysts for Hydrogen Production. *Catal. Today* **2012**, 197, 190–205.
133. Tentu, R. D.; Basu, S. Photocatalytic Water Splitting for Hydrogen Production. *Curr. Opin. Electrochem.* **2017**, 5 (1), 56–62.
134. Sultana, U. K.; Riches, J. D.; O'Mullane, A. P. Gold Doping in a Layered Co-ni Hydroxide System via Galvanic Replacement for Overall Electrochemical Water Splitting. *Adv. Funct. Mater.* **2018**, 1804361; <https://doi.org/10.1002/adfm.201804361>.
135. Kamaroddin, M. F. A.; Sabli, N.; Abdullah, T. A. T. Hydrogen Production by Membrane Water Splitting Technologies. In *Advances in hydrogen generation technologies*; Eyvaz, M., Ed. IntechOpen: London, UK, 2018, Ch. 2.
136. Rajeshwar, K. Hydrogen Generation at Irradiated Oxide Semiconductor - Solution Interfaces. *J. Appl. Electrochem.* **2007**, 37 (7), 765–787.
137. Gallo, A.; Marelli, M.; Psaro, R.; Gombac, V.; Montini, T.; Fornasiero, P.; Pievo, R.; Santo, V. D. Bimetallic Au-Pt/TiO₂ Photocatalysts Active under UV-A and Simulated Sunlight for H₂ Production from Ethanol. *Green Chem.* **2012**, 14, 330–333.
138. Lin, S.-Y.; Suzuki, Y.; Hatano, H.; Harada, M. Hydrogen Production from Hydrocarbon by Integration of Water-Carbon Reaction and Carbon Dioxide Removal (HyPr-RING Method). *Energy Fuel* **2001**, 15 (2), 339–343.
139. Abbas, H. F.; Wan Daud, W. M. A. Hydrogen Production by Methane Decomposition: A Review. *Int. J. Hydrog. Energy* **2010**, 35 (3), 1160–1190.
140. Rossetti, I. Hydrogen Production by Photoreforming of Renewable Substrates. *ISRN Chem. Eng.* **2012**, 1–21; <https://doi.org/10.5402/2012/964936>.
141. Caravaca, A.; Jones, W.; Hardacre, C.; Bowker, M. H₂ Production by the Photocatalytic Reforming of Cellulose and Raw Biomass Using Ni, Pd, Pt and Au on Titania. *Proc. Math. Phys. Eng. Sci.* **2016**, 472, 2191.
142. Cai, X.; Wang, C.; Chen, Y.; Cheng, Z.; Shu, R.; Zhang, J.; Bu, E.; Liao, M.; Song, Q. A Novel Approach for Enhancing Hydrogen Production from Bio-Glycerol Photoreforming by Improving Colloidal Dispersion Stability. *Sci. Total Environ.* **2018**, 627, 1464–1472.
143. Zhang, L.; Chen, R.; Luo, J.; Miao, J.; Gao, J.; Liu, B. Sustainable Hydrogen and Chemical Production via Photo-Electrochemical Reforming of Biomass-Derived Alcohols. *Nano Res.* **2016**, 9 (11), 3388–3393.
144. Kondarides, D. I.; Daskalaki, V. M.; Patsoura, A.; Verykios, X. E. Hydrogen Production by Photo-Induced Reforming of Biomass Components and Derivatives at Ambient Conditions. *Catal. Lett.* **2008**, 122 (1–2), 26–32.
145. Chen, G.; Xu, N.; Li, X.; Liu, Q.; Yang, H.; Li, W. Hydrogen Production by Aqueous-phase Reforming of Ethylene Glycol over a Ni/Zn/Al Derived Hydrotalcite Catalyst. *RSC Adv.* **2015**, 5, 60128–60134.
146. Meryemoglu, B.; Hasanoglu, A.; Kaya, B.; Irmak, S.; Erbatur, O. Hydrogen Production from Aqueous-phase Reforming of Sorghum Biomass: An Application of the Response Surface Methodology. *Renew. Energ.* **2014**, 62, 535–541.
147. Rahman, M. M. H₂ Production from Aqueous-phase Reforming of Glycerol over Cu-Ni Bimetallic Catalysts Supported on Carbon Nanotubes. *Int. J. Hydrog. Energy* **2015**, 40 (43), 14833–14844.
148. Vaidya, P. D.; Lopez-Sanchez, J. A. Review of Hydrogen Production by Catalytic Aqueous-phase Reforming. *Chem. Select.* **2017**, 2 (22), 6563–6567.
149. Chen, G.-Y.; Li, W.-Q.; Chen, H.; Yan, B.-B. Progress in the Aqueous-phase Reforming of Different Biomass-Derived Alcohols for Hydrogen Production. *J. Zhejiang Uni.-Sci. A.* **2015**, 16 (6), 491–506.

150. Cargnello, M.; Gasparotto, A.; Gombac, V.; Montini, T.; Barreca, D.; Fornasiero, P. Photocatalytic H₂ and Added-value By-products – the Role of Metal Oxide Systems in Their Synthesis from Oxygenates. *Eur. J. Inorg. Chem.* **2011**, 28, 4309–4323.
151. Vita, A.; Pino, L.; Italiano, C.; Palella, A. Steam Reforming, Partial Oxidation, and Autothermal Reforming of Ethanol for Hydrogen Production in Conventional Reactors. In *Ethanol: Science and Engineering*; Basile, A.; Iulianelli, A.; Dalena, F.; Veziroglu, T. N., Eds. Elsevier: Amsterdam, Netherlands, 2019; pp 159–191, Ch. 6.
152. Patcharavorachot, Y.; Wasuleewan, M.; Assabumrungrat, S.; Arpornwichean, A. Analysis of Hydrogen Production from Methane Autothermal Reformer with a Dual Catalyst-Bed Configuration. *Theor. Found. Chem. Eng.* **2012**, 46 (6), 658–665.
153. Geissler, K.; Newson, E.; Vogel, F.; Truong, T.-B.; Hottinger, P.; Wokaun, A. Autothermal Methanol Reforming for Hydrogen Production in Fuel Cell Applications. *Phys. Chem. Chem. Phys.* **2001**, 3, 289–293.
154. Niu, H.; Wang, Q.; Huang, C.; Zhang, M.; Yan, Y.; Liu, T.; Zhou, W. Noble Metal-Based Heterogeneous Catalysts for Electrochemical Hydrogen Evolution Reaction. *Appl. Sci.* **2023**, 13, 2177.
155. Donald, I. *Development of lanthanum-based heterogeneous catalysts for sustainable hydrogen production*. Thesis, Loughborough University, Loughborough, U.K, 2023; <https://doi.org/10.26174/thesis.lboro.24101373.v1>.
156. Nagaoka, K.; Eboshi, K.; Takeishi, Y.; Tasaki, R.; Honda, K.; Imamura, K.; Sato, K. Carbon-free H₂ Production from Ammonia Triggered at Room Temperature with an Acidic RuO₂/γ-La₂O₃ Catalyst. *Sci. Adv.* **2017**, 3; <https://doi.org/10.1126/sciadv.1602747>.
157. Li, Y.; Gao, X.; Iv, X.; Duan, Y.; Sui, D.; Chang, W.; Yang, Y. Recent Progress on Cobalt-Based Heterogeneous Catalysts for Hydrogen Production from Ammonia Borane. *ChemCatChem* **2024**, e202401271; <https://doi.org/10.1002/cctc.202401271>.
158. Brack, P.; Dann, S. E.; Wijayantha, K. G. U. Heterogeneous and Homogenous Catalysts for Hydrogen Generation by Hydrolysis of Aqueous Sodium Borohydride (NaBH₄) Solutions. *Energy Sci. Eng.* **2015**, 3 (3), 174–188.
159. Srifa, A.; Okura, K.; Okanishi, T.; Muroyama, H.; Matsui, T.; Eguchi, K. Hydrogen Production by Ammonia Decomposition over Cs-Modified Co₃Mo₃N Catalysts. *Appl. Catal. B Environ.* **2017**, 218, 1–8.
160. Yan, B.; Wu, J.; Xie, C.; He, F.; Wei, C. Supercritical Water Gasification with Ni/ZrO₂ Catalyst for Hydrogen Production from Model Wastewater of Polyethylene Glycol. *J. Supercrit. Fluids* **2009**, 50, 155–161.
161. Yuranov, I.; Autissier, N.; Sordakis, K.; Dalebrook, A.; Grasemann, M.; Orava, V.; Cendula, P.; Gubler, L.; Laurenczy, G. Heterogeneous Catalytic Reactor for Hydrogen Production from Formic Acid and its Use in Polymer Electrolyte Fuel Cells. *ACS Sus. Chem. Eng.* **2018**, 6 (5), 6635–6643.
162. Navlani-Garcia, M.; Mori, K.; Salinas-Torres, D.; Kuwahara, Y.; Yamashita, H. New Approaches toward the Hydrogen Production from Formic Acid Dehydrogenation over Pd-Based Heterogeneous Catalysts. *Front. Mater.* **2019**, 6, 44.
163. Navlani-Garcia, M.; Mori, K.; Kuwahara, Y.; Yamashita, H. Recent Strategies Targeting Efficient Hydrogen Production from Chemical Hydrogen Storage Materials over Carbon-Supported Catalysts. *NPG Asia Mater.* **2018**, 10, 277–292.
164. Yamaguchi, A.; Hiyoshi, N.; Sato, O.; Bando, K. K.; Shirai, M. Gaseous Fuel Production from Nonrecyclable Paper Wastes by Using Supported Metal Catalysts in High Temperature Liquid Water. *ChemSusChem* **2010**, 3, 737–741.
165. Sikander, U.; Sufian, S.; Salam, M. A. A Review of Hydrotalcite Based Catalysts for Hydrogen Production Systems. *Int. J. Hydrog. Energy* **2017**, 42, 19851–19868.
166. Daza, C. E.; Gallego, J.; Mondragon, F.; Moreno, S.; Molina, R. High Stability of Ce-Promoted Ni/Mg-Al Catalysts Derived from Hydrotalcites in Dry Reforming of Methane. *Fuel* **2010**, 89 (3), 592–603.
167. Khan, A. I.; O'Hare, D. Intercalation Chemistry of Layered Double Hydroxides: Recent Developments and Applications. *J. Mater. Chem.* **2002**, 12 (11), 3191–3198.
168. Ota, A.; Kunkes, E. L.; Kasatkin, I.; Groppo, E.; Ferri, D.; Poceiro, B.; Navarro Yerga, R. M.; Behrens, M. Comparative Study of Hydrotalcite-Derived Supported Pd₂Ga and PdZn Intermetallic Nanoparticles as Methanol Synthesis and Methanol Steam Reforming Catalysts. *J. Catal.* **2012**, 293 (0), 27–38.
169. Lenarda, M.; Storaro, L.; Frattini, R.; Casagrande, M.; Marchiori, M.; Capannelli, G.; Uliana, C.; Ferrari, F.; Ganzerla, R. Oxidative Methanol Steam Reforming (OSRM) on a PdZnAl Hydrotalcite Derived Catalyst. *Catal. Commun.* **2007**, 8 (3), 467–470.
170. Contreras, J.; Tapia, C.; Fuentes, G.; Nuno, L.; Quintana, B.; Salmones, J.; Zeifert, B.; Córdova, I. Equilibrium Composition of Ethanol Steam Reforming Reaction to Produce H₂ Applied to Ni, Co and Pt/ hydrotalcites-WO_x Catalysts. *Int. J. Hydrog. Energy* **2014**, 39 (29), 16608–16618.
171. Li, D.; Shishido, T.; Oumi, Y.; Sano, T.; Takehira, K. Self-activation and Self-Regenerative Activity of Trace Rh-Doped Ni/Mg(Al)O Catalysts in Steam Reforming of Methane. *Appl. Catal. Gen.* **2007**, 332 (1), 98–109.
172. Sikander, U.; Samsudin, M. F.; Sufian, S.; KuShari, K.; Kait, C. F.; Naqvi, S. R.; Chen, W.-S. Tailored Hydrotalcite-Based Mg-Ni-Al Catalyst for Hydrogen Production via Methane Decomposition: Effect of Nickel Concentration and Spinel-like Structures. *Int. J. Hydrog. Energy* **2018**, 42, 19851–19868.
173. Dewoolkar, K. D.; Vaidya, P. D. Improved Hydrogen Production by Sorption-Enhanced Steam Methane Reforming over Hydrotalcite- and Calcium-Based Hybrid Materials. *Energy. Fuel.* **2015**, 29, 3870–3878.
174. Abello, S.; Bolshak, E.; Montane, D. Ni-Fe Catalysts Derived from Hydrotalcite-like Precursors for Hydrogen Production by Ethanol Steam Reforming. *Appl. Catal. A: Gen.* **2013**, 450, 261–274.
175. He, L.; Huang, Y.; Wang, A.; Wang, X.; Chen, X.; Jose, J.; Delgado, Z. T. A Noble-metal-free Catalyst Derived from Ni-Al Hydrotalcite for Hydrogen Generation from N₂H₄·H₂O Decomposition. *Angew. Chem. Int. Ed.* **2012**, 51, 1–5.
176. Homs, D.; Aouad, S.; Gennequin, C.; Aboukais, A.; Abi-Aad, E. Hydrogen Production by Methane Steam Reforming over Ru and Cu Supported on Hydrotalcite Precursors. *Adv. Mater. Res.* **2011**, 324, 453–456.
177. Homs, D.; Rached, J. A.; Aouad, S.; Gennequin, C.; Dahdah, E.; Estephane, J.; Tidahy, H. L.; Aboukais, A.; Abi-Aad, E. Steam Reforming of Ethanol for Hydrogen Production over Cu/Co-Mg-Al-Based Catalysts Prepared by Hydrotalcite Route. *Environ. Sci. Pollut. Res.* **2016**, 24 (11), 9907–9913.
178. Tuza, P. V.; Manfro, R. L.; Ribeiro, N. F. P.; Souza, M. M. V. M. Production of Renewable Hydrogen by Aqueous-phase Reforming of Glycerol over Ni-Cu Catalysts Derived from Hydrotalcite Precursors. *Renew. Energy.* **2013**, 50, 408–414.
179. (a) Liang, X.; Wang, C.; Lei, Y.; Liu, Y.; Zhao, B.; Liu, F. Potential Applications of Metal Organic Framework-Based Materials for Proton Exchange Membrane Fuel Cells. *Progr. Chem* **2018**, 30 (11), 1770–1783. (b) Si, G. R.; Yang, F.; He, T.; Kong, X. J.; Wu, W.; Li, T. C.; Wang, K.; Li, J. R. Enhancing Proton Conductivity in Zr-MOFs through

- Tuning Metal Cluster Connectivity. *J. Mater. Chem. A* **2022**, *10*, 1236–1240.(c) Feng, L.; Hou, H.-B.; Zhou, H. UiO-66 Derivatives and Their Composite Membranes for Effective Proton Conduction. *Dalton Trans.* **2020**, *49*, 17130–17139.(d) Choi, I.; Lim, J.; dos Reis, R.; Kim, E.; Lim, S. Y.; Dravid, V. P.; Kim, H.; Oh, K.-H.; Nam, K. W. Metal-organic Framework for High-Performance Catalyst Layers in Proton-Exchange Membrane Fuel Cells. *J. Mater. Chem. A* **2023**, *11*, 20583–20591.(e) Parangi, T. F.; Chudasama, U. V. Synthesis, Characterization, and Proton Conduction Behavior of Thorium and Cerium Phosphonates. *ACS Omega* **2019**, *4* (2), 3716–3725.
180. (a) Jiang, Y.; Zhao, H.; Yue, L.; Liang, J.; Li, T.; Liu, Q.; Luo, Q.; Kong, X.; Lu, S.; Shi, X.; Zhou, K.; Sun, X. Recent Advances in Lithium-Based Batteries Using Metal Organic Frameworks as Electrode Materials. *Electrochem. Commun.* **2021**, *122*, 122.(b) Zhao, R.; Liang, Z.; Zou, R.; Xu, Q. Metal-organic Frameworks for Batteries. *Joule* **2018**, *2* (11), 2235–2259.(c) Nam, K. W.; Park, S. S.; dos Reis, R.; Vinayak, P.; Kim, H.; Mirkkin, C. A.; Stoddart, J. F. Conductive 2D Metal-Organic Framework for High-Performance Cathodes in Aqueous Rechargeable Zinc Batteries. *Nat. Commun.* **2019**, *10*, 4948.(d) Mehek, R.; Iqbal, N.; Noor, T.; Amjad, Z. B.; Ali, G.; Vignaroobanc, K.; Khan, M. A. Metal-organic Framework Based Electrode Materials for Lithium-Ion Batteries: A Review. *RSC Adv.* **2021**, *11*, 29247–29266.(e) Yin, C.; Xu, F.; Pan, Y.; Pan, C. Metal-organic Framework as Anode Materials for Lithium-Ion Batteries with High Capacity and Rate Performance. *ACS Appl. Energy Mater.* **2020**, *3* (11), 10776–10786.(f) Tran, A.; Do, H. H.; Ha, D. C.; Ahn, S.; Kim, M.-G.; Kim, S. Y.; Lee, S.-W. Metal-organic Framework for Lithium and Sodium-Ion Batteries: Progress and Perspective. *Fuel* **2022**, *319*.
 181. Muntean, M.; Guizzardi, D.; Schaaf, E.; Crippa, M.; Solazzo, E.; Olivier, J. G. J.; Vignati, E. *Fossil CO₂ emissions of all world countries – Report, EUR 29433 EN*; Publications Office of the European Union: Luxembourg, 2018.
 182. Perez-Fortes, M.; Tzimas, E. European Commission. In *Carbon Capture Utilisation and Storage*; SETIS, Luxemburg, U.K., 2016.
 183. Juan, G.-S.; Raul, P.-H.; Desiree, D.-M. Inspirational Perspectives and Principles on the Use of Catalysts to Create Sustainability. *Catal. Today* **2022**, *387*, 237–243.
 184. Bahruji, H.; Bowker, M.; Hutchings, G.; Dimitratos, N.; Wells, P.; Gibson, E.; Jones, W.; Brookes, C.; Morgan, D.; Lalev, G. Pd/ZnO Catalysts for Direct CO₂ Hydrogenation to Methanol. *J. Catal.* **2016**, *343*, 133–146.
 185. Pastor-Perez, L.; Baibars, F.; Sache, E. L.; Arellano-Garcia, H.; Gu, S.; Reina, T. R. CO₂ Valorisation via Reverse Water-Gas Shift Reaction Using Advanced Cs Doped Fe-Doped Cu/Al₂O₃ Catalysts. *J. CO₂ Util.* **2017**, *21*, 423–428.
 186. Stroud, T.; Smith, T.; Sache, S. L.; Santos, J. L.; Centeno, M. A.; Arellano-Garcia, H.; Odriozola, J. A.; Reina, T. R. Chemical CO₂ Recycling via Dry and Bi Reforming of Methane Using Ni-Sn/Al₂O₃ and Ni-Sn/CeO₂-Al₂O₃ Catalysts. *Appl. Catal. B Environ.* **2018**, *225*, 125–137.
 187. Mutz, B.; Belimov, M.; Wang, W.; Sprenger, P.; Serrer, M.-A.; Wang, D.; Pfeifer, P.; Kleist, W.; Grunwaldt, J.-D. Potential of an Alumina-Supported Ni₃Fe Catalyst in the Methanation of CO₂: Impact of Alloy Formation on Activity and Stability. *ACS Catal.* **2017**, *7*, 6802–6814.
 188. Li, W.; Nie, X.; Jiang, X.; Zhang, A.; Ding, F.; Liu, M.; Liu, Z.; Guo, X.; Song, C. ZrO₂ Support Imparts Superior Activity and Stability of Co Catalysts for CO₂ Methanation. *Appl. Catal. B Environ.* **2018**, *220*, 397–408.
 189. Veselovskaya, J. V.; Parunin, P. D.; Okunev, A. G. Catalytic Process for Methane Production from Atmospheric Carbon Dioxide Utilizing Renewable Energy. *Catal. Today* **2017**, *298*, 117–123.
 190. Wu, P.; Yang, B. Significance of Surface Formate Coverage on the Reaction Kinetics of Methanol Synthesis from CO₂ Hydrogenation over Cu. *ACS Catal.* **2017**, *7* (10), 7187–7195.
 191. Wu, C.; Zhang, P.; Zhang, Z.; Zhang, L.; Yang, G.; Han, B. Efficient Hydrogenation of CO to Methanol over Supported Subnanometric Gold Catalysts at Low Temperature. *ChemCatChem* **2017**, *9* (19), 3691–3696.
 192. Garcia-Trenco, A.; Regoutz, A.; White, E. R.; Payne, D. J.; Shaffer, M. S. P.; Williams, C. K. PdIn Intermetallic Nanoparticles for the Hydrogenation of CO₂ to Methanol. *Appl. Catal. B Environ.* **2018**, *220*, 9–18.
 193. Meher, S. K.; Rao, G. R. Nanostructured CeO₂ as Efficient Catalyst for Energy and Environmental Applications. *J. Chem. Sci.* **2014**, *126* (2), 361–372.
 194. Arena, F. 3Multipurpose Composite MnCeO_x Catalysts for Environmental Applications. *Cat. Sci. Technol.* **2014**, *4* (7), 1890–1898.
 195. Jadhav, S. G.; Vaidya, P. D.; Bhanage, B. M.; Joshi, J. B. Catalytic Carbon Dioxide Hydrogenation to Methanol: A Review of Recent Studies. *Chem. Eng. Res. Design.* **2014**, *92*, 2557–2567.
 196. Liang, X. L.; Dong, X.; Lin, G. D.; Zhang, H. B. Carbon Nanotube-Supported Pd-ZnO Catalyst for Hydrogenation of CO₂ to Methanol. *Appl. Catal. B Environ.* **2009**, *88*, 315–322.
 197. Bonivardi, A. L.; Chiavassa, D. L.; Querini, C. A.; Baltanas, M. A. Enhancement of the Catalytic Performance to Methanol Synthesis from CO₂/H₂ by Gallium Addition to Palladium/silica Catalysts. *Stud. Surf. Sci. Catal.* **2000**, *130*, 3747–3752.
 198. Porosoff, M. D.; Yang, X.; Boscoboinik, J. A.; Chen, J. G. Molybdenum Carbide as Alternative Catalysts to Precious Metals for Highly Selective Reduction of CO₂ to CO. *Angew. Chem. Int. Ed.* **2014**, *53* (26), 6705–6709.
 199. DeO7, S.; Zhang, J.; Luque, R.; Yan, N. Ni-based Bimetallic Heterogeneous Catalysts for Energy and Environmental Applications. *Energy. Environ. Sci.* **2016**, *9*, 3314–3347.
 200. Labhasetwar, N.; Saravanan, G.; Megarajan, S. K.; Manwar, N.; Khobragade, P. D.; Grasset, F.; Grasset, F. Perovskite-type Catalytic Materials for Environmental Applications. *Sci. Technol. Adv. Mater.* **2015**, *16*; <https://doi.org/10.1088/1468-6996/16/3/036002>.
 201. Wang, S. Application of Solid Ash Based Catalysts in Heterogeneous Catalysis. *Environ. Sci. Technol.* **2008**, *42*, 7055–7063.
 202. Wang, N.; Zhao, Q.; Zhang, A. Catalytic Oxidation of Organic Pollutants in Wastewater via a Fenton-like Process under the Catalysis of HNO₃-Modified Coal Fly Ash. *RSC Adv.* **2017**, *7*, 27619–27628.
 203. (a) Stanley, P. M.; Ramm, V.; Fischer, R. A.; Warnan, J. Analysis of Metal–Organic Framework-Based Photosynthetic CO₂ Reduction. *Nat. Synth.* **2024**, *3*, 307–318.(b) Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T.-H.; Long, J. R. Carbon Dioxide Capture in Metal–Organic Frameworks. *Chem. Rev.* **2012**, *112* (2), 724–781.(c) Trickett, C.; Helal, A.; Al-Maythaly, B.; Yamani, Z. H.; Cordova, K. E.; Yaghi, O. M. The Chemistry of Metal–Organic Frameworks for CO₂ Capture, Regeneration and Conversion. *Nat. Rev. Mater.* **2017**, *2*, 17045.(d) Mahajan, S.; Lahtinen, M. Recent Progress in Metal-Organic Frameworks (MOFs) for CO₂ Capture at Different Pressures. *J. Environ. Chem. Eng.* **2022**, *10* (6).(e) Chen, Y.; Wang, D.; Deng, X.; Li, Z. Metal–organic Frameworks (MOFs) for Photocatalytic CO₂ Reduction. *Catal. Sci. Technol.* **2017**, *7*, 4893–4904.
 204. (a) Mtukula, A. C.; Zhang, X.-D.; Hou, S.-Z.; Huang, J.-M.; Xu, M.; Gu, Z.-Y. Metal-organic Frameworks for Efficient Electrochemical Reduction of Carbon Dioxide. *Eur. J. Inorg. Chem.* **2024**, *26* (21), 202300170.(b) Kornienko, N.; Zhao, Y.; Kley, C. S.; Zhu, C.; Kim, D.; Lin, S.; Chang, C. J.; Yaghi, O. M.; Yang, P. Metal–organic Frameworks for Electrocatalytic Reduction of Carbon Dioxide. *J. Am. Chem. Soc.* **2015**,

- 137 (44), 14129–14135.(c) Yao, D.; Tang, C.; Vasileff, A.; Zhi, X.; Jiao, Y.; Qiao, S.-Z. The Controllable Reconstruction of Bi-MOFs for Electrochemical CO₂ through Electrolyte and Potential Mediation. *Angew. Chem. Int. Ed.* **2021**, 60 (33), 18178–18184.(d) Zhang, C.; Lin, Z.; Jiao, L.; Jiang, H.-L. Metal–organic Frameworks for Electrocatalytic CO₂ Reduction: From Catalytic Site Design to Microenvironment Modulation. *Angew. Chem. Int. Ed.* **2024**, 60 (33), 202414506.
205. Li, X.-X.; Liu, J.; Zhang, L.; Dong, L.-Z.; Xin, Z.-F.; Li, S.-L.; Huang-Gu, X.-Q.; Huang, K.; Lan, Y.-Q. Hydrophobic Polyoxometalate-Based Metal-Organic Framework for Efficient CO₂ Photoconversion. *ACS Appl. Mater. Interfaces* **2019**, 11 (29), 25790–25795.
206. Lee, Y.; Kim, S.; Kang, J. K.; Cohen, S. M. Photocatalytic CO₂ Reduction by a Mixed Metal (Zr/Ti), Mixed Ligand Metal-Organic Framework under Visible Light Irradiation. *Chem. Commun.* **2015**, 51 (26), 5735–5738.
207. Acharya, R.; Naik, B.; Parida, K. Cr(VI) Remediation from Aqueous Environment through Modified-TiO₂-Mediated Photocatalytic Reduction. *Beilstein J. Nanotechnol.* **2018**, 9, 1448–1470.
208. Mahlambi, M. M.; Ngila, C. J.; Mamba, B. B. Recent Developments in Environmental Photocatalytic Degradation of Organic Pollutants: the Case of Titanium Dioxide Nanoparticles – A Review. *J. Nanomater.* **2015**, 29, 790173.
209. Byrne, C.; Subramanian, G.; Pillai, S. C. Recent Advances in Photocatalysis for Environmental Applications. *J. Environ. Chem. Eng.* **2018**, 6, 3531–3555.
210. Phonsy, P. D.; Anju, S. G.; Jyothi, K. P.; Yesodharan, S.; Yesodharan, E. P. Semiconductor Mediated Photocatalytic Degradation of Plastics and Recalcitrant Organic Pollutants in Water: Effect of Additives and Fate of *In situ* Formed H₂O₂. *J. Adv. Oxid. Technol.* **2015**, 18 (1); <https://doi.org/10.1515/jaots-2015-0111>.
211. Khader, E. M.; Muslim, S. A.; Saady, N. M. C.; Ali, N. S.; Salih, I. K.; Mohammed, T. J.; Albayati, T. M.; Zendeheboudi, S. Recent Advances in Photocatalytic Advanced Oxidation Processes for Organic Compound Degradation: A Review. *Desalination Water Treat.* **2024**, 318; <https://doi.org/10.1016/j.dwt.2024.100384>.
212. (a) Huang, N.; Wang, T.; Wang, W.; Wu, Q.; Li, A.; Hu, H. UV/chlorine as an Advanced Oxidation Process for the Degradation of Benzalkonium Chloride: Synergistic Effect, Transformation Products and Toxicity Evaluation. *Water Res.* **2017**, 114, 246–253.(b) Ferkous, H.; Merouani, S.; Hamdaoui, O.; Petrier, C. Persulfate-enhanced Sonochemical Degradation of Naphthol Blue Black in Water: Evidence of Sulfate Radical Formation. *Ultrason. Sonochem.* **2017**, 34, 580–587.(c) Chadi, N. E.; Merouani, S.; Hamdaoui, O.; Bouhelassa, M.; Ashokkumar, M. H₂O₂/Periodate (IO₄⁻): A Novel Advanced Oxidation Technology for the Degradation of Refractory Organic Pollutants. *Environ. Sci. Water Res. Technol.* **2019**, 5, 1113–1123.
213. Duan, X.; Wang, S. Heterogeneous Catalysis for Environmental Remediation. *Catalysts* **2017**, 7, 236.
214. Wang, Y.; Xie, Y.; Chen, C.; Duan, X.; Sun, H.; Wang, S. Synthesis of Magnetic Carbon Supported Manganese Catalysts for Phenol Oxidation by Activation of Peroxymonosulfate. *Catalysts* **2017**, 7, 3.
215. Zhu, K.; Jin, C.; Klencsar, Z.; Ganeshraja, A.; Wang, J. Cobalt-iron Oxide, Alloy and Nitride: Synthesis, Characterization and Application in Catalytic Peroxymonosulfate Activation for Orange II Degradation. *Catalysts* **2017**, 7, 138.
216. Chen, C.; Chen, Y.; Yoza, B.; Du, Y.; Wang, Y.; Li, Q.; Yi, L.; Guo, S.; Wang, Q. Comparison of Efficiencies and Mechanisms of Catalytic Ozonation of Recalcitrant Petroleum Refinery Wastewater by Ce, Mg, and Ce-Mg Oxides Loaded Al₂O₃. *Catalysts* **2017**, 7, 72.
217. Wang, Y.; Wen, Z.; Zhang, H.; Cao, G.; Sun, Q.; Cao, J. CuO Nanorods-Decorated Reduced Graphene Oxide Nanocatalysts for Catalytic Oxidation of CO. *Catalysts* **2016**, 6, 214.
218. Stahl, A.; Wang, Z.; Schwammle, T.; Ke, J.; Li, X. Novel Fe-W-Ce Mixed Oxide for the Selective Catalytic Reduction of NO_x with NH₃ at Low Temperatures. *Catalysts* **2017**, 7, 71.
219. Qi, C.; Bao, W.; Wang, L.; Li, H.; Wu, W. Study of the V₂O₅-WO₃/TiO₂ Catalyst Synthesized from Waste Catalyst on Selective Catalytic Reduction of NO_x by NH₃. *Catalysts* **2017**, 7, 110.
220. Zhang, Y.; Kumar Megarajan, S.; Xu, X.; Lu, J.; Jiang, H. Catalytic Abatement of Nitrous Oxide Coupled with Ethane Oxydehydrogenation over Mesoporous Cr/Al₂O₃ Catalyst. *Catalysts* **2017**, 7, 137.
221. Zheng, X.; Zhang, R.; Bai, F.; Hua, C. Catalytic Decomposition of N₂O over Cu-Zn/ZnAl Catalysts. *Catalysts* **2017**, 7, 166.
222. Muhammad, S.; Saputra, E.; Sun, H.; Ang, H. M.; Tade, M. O.; Wang, W. Heterogeneous Catalytic Oxidation of Aqueous Phenol on Red Mud Supported Cobalt Catalysts. *Ind. Eng. Chem. Res.* **2012**, 51, 15351–15359.
223. Muhammad, S.; Saputra, E.; Sun, H.; Ang, H. M.; Tade, M. O.; Wang, W. Removal of Phenol Using Sulphate Radicals Activated by Natural Zeolite-Supported Cobalt Catalysts. *Water Air Soil Pollut.* **2013**, 224, 1721.
224. Jain, B.; Singh, A. K.; Kim, H.; Lichtfouse, E.; Sharma, V. K. Treatment of Organic Pollutants by Homogeneous and Heterogeneous Fenton Reaction Processes. *Environ. Chem. Lett.* **2018**, 16 (3), 947–967.
225. Saputra, E.; Muhammad, S.; Sun, H.; Wang, S.; Ang, H.-A.; Tade, M. O.; Wang, S. A Comparative Study of Spinel Structured Mn₃O₄, Co₃O₄ and Fe₃O₄ Nanoparticles in Catalytic Oxidation of Phenolic Contaminants in Aqueous Solutions. *J. Coll. Interface Sci.* **2013**, 407, 467–473.
226. Saputra, E.; Muhammad, S.; Sun, H.; Wang, S. Activated Carbons as Green and Effective Catalysts for Generation of Reactive Radicals in Degradation of Aqueous Phenol. *RSC Adv.* **2013**, 3, 21905–21910.
227. Galeano, L.-A.; Vicente, M. A.; Gil, A. Catalytic Degradation of Organic Pollutants in Aqueous Streams by Mixed Al/M-Pillared Clays (M = Fe, Cu, Mn). *Catal. Rev. Sci. Eng.* **2014**, 56 (3), 239–287.
228. Kurian, M.; Nair, D. Manganese Zinc Ferrite Nanoparticles as Efficient Catalysts for Wet Peroxide Oxidation of Organic Aqueous Wastes. *J. Chem. Sci.* **2015**, 127 (3), 537–546.
229. Wang, N.; Zhao, Q.; Zhang, A. Catalytic Oxidation of Organic Pollutants in Wastewater via a Fenton-like Process under the Catalysis of HNO₃-Modified Coal Fly Ash. *RSC Adv.* **2017**, 7, 27619–27628.
230. Zhen, M. Cobalt Oxide Catalysts for Environmental Remediation. *Curr. Catal.* **2014**, 3, 15–26.
231. Gangarajula, Y.; Gopal, B. Spinel Cobalt Oxide Catalyzed Controlled Hydration of Aromatic Nitriles. *Chem. Lett.* **2012**, 41, 101–103.
232. Davies, T. E.; García, T.; Solsona, B.; Taylor, S. H. Nanocrystalline Cobalt Oxide: A Catalyst for Selective Alkane Oxidation under Ambient Conditions. *Chem. Commun.* **2006**, 3417–3419; <https://doi.org/10.1039/b606973h>.
233. Tyo, E. C.; Yin, C. R.; Vece, M. D.; Qian, Q.; Kwon, G.; Lee, S.; Lee, B.; DeBartolo, J. E.; Seifert, S.; Winans, R. E.; Si, R.; Ricks, B.; Goergen, S.; Rutter, M.; Zugic, B.; Flytzani-Stephanopoulos, M.; Wang, Z. W.; Palmer, R. E.; Neurock, M.; Vajda, S. Oxidative Dehydrogenation of Cyclohexane on Cobalt Oxide (Co₃O₄) Nanoparticles: The Effect of Particle Size on Activity and Selectivity. *ACS Catal.* **2012**, 2, 2409–2423.
234. Mangrulkar, P. A.; Joshi, M. M.; Tijare, S. N.; Polshettiwar, V.; Labhsetwar, N. K.; Rayalu, S. S. Nano Cobalt Oxides for Photocatalytic Hydrogen Production. *Int. J. Hydrogen Energ.* **2012**, 37, 10462–10466.

235. Kumar, A.; Rana, A.; Sharma, G.; Sharma, S.; Naushad, M.; Mola, G. T.; Dhiman, P.; Stadler, F. J. Aerogels and Metal-Organic Frameworks for Environmental Remediation and Energy Production. *Environ. Chem. Lett.* **2018**, 16 (3), 797–820.
236. Chen, P.; Wang, H.; Liu, H.; Ni, Z.; Li, J.; Zhou, Y.; Dong, F. Directional Electron Delivery and Enhanced Reactants Activation Enable Efficient Photocatalytic Air Purification on Amorphous Carbon Nitride Co-functionalized with O/La. *Appl. Catal. B Environ.* **2019**, 242, 19–30.
237. Dong, X.; Li, J.; Xing, Q.; Zhou, Y.; Huang, H.; Dong, F. The Activation of Reactants and Intermediates Promotes the Selective Photocatalytic NO Conversion on Electron-Localized Sr-Intercalated G-C₃N₄. *Appl. Catal. B Environ.* **2018**, 232, 69–76.
238. Cui, W.; Li, J.; Sun, Y.; Wang, H.; Jiang, G.; Lee, S. C.; Dong, F. Enhancing ROS Generation and Suppressing Toxic Intermediate Production in Photocatalytic NO Oxidation on O/Ba Co-functionalized Amorphous Carbon Nitride. *Appl. Catal. B Environ.* **2018**, 237, 938–946.
239. Huo, W. C.; Dong, X.; Li, J. Y.; Liu, M.; Liu, X. Y.; Zhang, Y. X.; Dong, F. Synthesis of Bi₃WO₆ with Gradient Oxygen Vacancies for Highly Photocatalytic NO Oxidation and Mechanism Study. *Chem. Eng. J.* **2019**, 361, 129–138.
240. Cheng, L.; Xiang, Q.; Liao, Y.; Zhang, H. CdS-based Photocatalysts. *Energy Environ. Sci.* **2018**, 11, 1362–1391.
241. Lang, D.; Xiang, Q.; Qiu, G.; Feng, X.; Liu, F. Effects of Crystalline Phase and Morphology on the Visible Light Photocatalytic H₂-Production Activity of CdS Nanocrystals. *Dalton Trans.* **2014**, 43, 7245–7253.
242. Zhang, L.; Fu, X.; Meng, S.; Jiang, X.; Wang, J.; Chen, S. Ultra-low Content of Pt Modified CdS Nanorods: One-Pot Synthesis and High Photocatalytic Activity for H₂ Production under Visible Light. *J. Mater. Chem. A* **2015**, 3, 23732–23742.
243. Ma, D.; Shi, J. W.; Zou, Y.; Fan, Z.; Ji, X.; Niu, C. Highly Efficient Photocatalyst Based on a CdS Quantum dots/ZnO Nanosheets 0D/2D Heterojunction for Hydrogen Evolution from Water Splitting. *ACS Appl. Mater. Interfaces* **2017**, 9, 25377–25386.
244. (a) Daghrir, R.; Drogui, P.; Robert, D. Modified TiO₂ for Environmental Photocatalytic Applications: A Review. *Ind. Eng. Chem. Res.* **2013**, 52, 3581–3599. (b) Parangi, T.; Mishra, M. K. Titania Nanoparticles as Modified Photocatalysts: A Review on Design and Development. *Comments Inorg. Chem.* **2019**, 39, 90–126.
245. Kim, J. C.; Choi, J.; Lee, Y. B.; Hong, J. H.; Lee, J. I.; Yang, J. W.; Lee, W. I.; Hur, N. H. Enhanced Photocatalytic Activity in Composites of TiO₂ Nanotubes and CdS Nanoparticles. *Chem. Commun.* **2006**, 5024–5026; <https://doi.org/10.1039/b612572g>.
246. Cao, A.; Liu, Z.; Chu, S.; Wu, M.; Ye, Z.; Cai, Z.; Chang, Y.; Wang, S.; Gong, Q.; Liu, Y. A Facile One-step Method to Produce Graphene-CdS Quantum Dot Nanocomposites as Promising Optoelectronic Materials. *Adv. Mater.* **2010**, 22 (1), 103–106.
247. Cheng, F.; Xiang, Q. A Solid-State Approach to Fabricate a CdS/CuS Nano-Heterojunction with Promoted Visible-Light Photocatalytic H₂-Evolution Activity. *RSC Adv.* **2016**, 6, 76269–76272.
248. Jiang, D.; Sun, Z.; Jia, H.; Lu, D.; Du, P. A Cocatalyst-free CdS nanorod/ZnS Nanoparticle Composite for High-Performance Visible-Light-Driven Hydrogen Production from Water. *J. Mater. Chem. A* **2016**, 4, 675–683.
249. Hao, L. X.; Chen, G.; Yu, Y. G.; Zhou, Y. S.; Han, Z. H.; Liu, Y. Sonochemistry Synthesis of Bi₂S₃/CdS Heterostructure with Enhanced Performance for Photocatalytic Hydrogen Evolution. *Int. J. Hydrogen Energy* **2014**, 39, 14479–14486.
250. Bankar, P. K.; Pawar, M. S.; Pawbake, A. S.; Warule, S. S.; Late, D. J.; More, M. A. Spatially Branched CdS-Bi₂S₃ Heteroarchitecture: Single Step Hydrothermal Synthesis Approach with Enhanced Field Emission Performance and Highly Responsive Broadband Photodetection. *RSC Adv.* **2016**, 6, 95092–95100.
251. Zhong, Y.; Zhao, G.; Ma, F.; Wu, Y.; Hao, X. Utilizing Photocorrosion-Recrystallization to Prepare a Highly Stable and Efficient CdS/WS₂ Nanocomposite Photocatalyst for Hydrogen Evolution. *Appl. Catal. B Environ.* **2016**, 199, 466–472.
252. Yin, X. L.; Li, L. L.; Jiang, W. J.; Zhang, Y.; Zhang, X.; Wan, L. J.; Hu, J. S. MoS₂/CdS Nanosheets-On-Nanorod Heterostructure for Highly Efficient Photocatalytic H₂ Generation under Visible Light Irradiation. *ACS Appl. Mater. Interfaces* **2016**, 8, 15258–15266.
253. Xiang, Q. J.; Cheng, F. Y.; Lang, D. Hierarchical Layered WS₂/graphene-Modified CdS Nanorods for Efficient Photocatalytic Hydrogen Evolution. *ChemSusChem* **2016**, 9, 996–1002.
254. Jia, T.; Kolpin, A.; Ma, C.; Chan, R. C. T.; Kwok, W. M.; Tsang, S. C. E. A Graphene Dispersed CdS-MoS₂ Nanocrystal Ensemble for Cooperative Photocatalytic Hydrogen Production from Water. *Chem. Commun.* **2014**, 50, 1185–1188.
255. Chang, K.; Mei, Z.; Wang, T.; Kang, Q.; Ouyang, S.; Ye, J. MoS₂/graphene Cocatalyst for Efficient Photocatalytic H₂ Evolution under Visible Light Irradiation. *ACS Nano* **2014**, 8, 7078–7087.
256. Yang, M.-Q.; Han, C.; Xu, Y.-J. Insight into the Effect of Highly Dispersed MoS₂ versus Layer-Structured MoS₂ on the Photocorrosion and Photoactivity of CdS in Graphene-CdS-MoS₂ Composites. *J. Phys. Chem. C* **2015**, 119, 27234–27246.
257. Cheng, F.; Yin, H.; Xiang, Q. Low-temperature Solid-State Preparation of Ternary CdS/g-C₃N₄/CuS Nanocomposites for Enhanced Visible-Light Photocatalytic H₂-Production Activity. *Appl. Surf. Sci.* **2017**, 391, 432–439.
258. Neelgund, G. M.; Oki, A. Photocatalytic Activity of CdS and Ag₂S Quantum Dots Deposited on Poly(amidoamine) Functionalized Carbon Nanotubes. *Appl. Catal. B Environ.* **2011**, 110, 99–107.
259. Pan, Y. X.; Zhou, T.; Han, J.; Hong, J.; Wang, Y.; Zhang, W.; Xu, R. CdS Quantum Dots and Tungsten Carbide Supported on Anatase-Rutile Composite TiO₂ for Highly Efficient Visible-Light-Driven Photocatalytic H₂ Evolution from Water. *Catal. Sci. Technol.* **2016**, 6, 2206–2213.
260. Wang, L.; Duan, X.; Wang, G.; Liu, C.; Luo, S.; Zhang, S.; Zeng, Y.; Xu, Y.; Liu, Y.; Duan, X. Omnidirectional Enhancement of Photocatalytic Hydrogen Evolution over Hierarchical “Cauline Leaf” Nanoarchitectures. *Appl. Catal. B Environ.* **2016**, 186, 88–96.
261. Yu, J.; Jin, J.; Cheng, B.; Jaroniec, M. A Noble Metal-free Reduced Graphene Oxide-CdS Nanorod Composite for the Enhanced Visible-Light Photocatalytic Reduction of CO₂ to Solar Fuel. *J. Mater. Chem. A* **2014**, 2, 3407–3416.
262. Tian, Q.; Wu, W.; Liu, J.; Wu, Z.; Yao, W.; Ding, J.; Jiang, C. Dimensional Heterostructures of 1D CdS/2D ZnIn₂S₄ Compositing with 2D Graphene: Designed Synthesis and Superior Photocatalytic Performance. *Dalton Trans.* **2017**, 46, 2770–2777.
263. Xie, Y.; Ali, G.; Yoo, S. H.; Cho, S. O. Sonication-assisted Synthesis of CdS Quantum-Dot-Sensitized TiO₂ Nanotube Arrays with Enhanced Photoelectrochemical and Photocatalytic Activity. *ACS Appl. Mater. Interfaces* **2010**, 2, 2910–2914.
264. Fujishima, A.; Honda, K. Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* **1972**, 238, 37–38.
265. Ma, Y.; Wang, X.; Jia, Y.; Chen, X.; Han, H.; Li, C. Titanium Dioxide-Based Nanomaterials for Photocatalytic Fuel Generations. *Chem. Rev.* **2014**, 114, 9987–10043.
266. Asahi, R.; Morikawa, T.; Irie, H.; Ohwaki, T. Nitrogen-doped Titanium Dioxide as Visible-Light-Sensitive Photocatalyst: Designs, Developments, and Prospects. *Chem. Rev.* **2014**, 114, 9824–9852.

267. Dahl, M.; Liu, Y.; Yin, Y. Composite Titanium Dioxide Nanomaterials. *Chem. Rev.* **2014**, *114*, 9853–9889.
268. Liu, L.; Chen, X. Titanium Dioxide Nanomaterials: Self-Structural Modifications. *Chem. Rev.* **2014**, *114*, 9890–9918.
269. (a) Yohannes, A.; Su, Y.; Yao, S. Emerging Applications of Metal–Organic Frameworks for Environmental Remediation. In: *Metal–Organic Frameworks for Environmental Remediation*; Ghosh, P.; Kumar, S. S.; Singh, L. Eds.; ACS, USA, Vol. 1395, Ch. 1, **2021**; p. 1–23. (b) Kumar, A.; Kumar, S.; Duhan, S.; Kumar, A.; Devi, S.; Kumar, P. Environmental Applications of Metal–organic Frameworks, In: *Metal–organic frameworks for environmental remediation*, Ghosh, P.; Kumar, S. S.; Singh, L. Eds.; ACS, USA, Vol. 1395, Ch. 10, **2021**, pp. 247–255. (c) Jang, S.; Song, S.; Lim, J. H.; Kim, H. S.; Phan, B. T.; Ha, K.-T.; Park, S.; Park, K. H. Application of Various Metal-Organic Frameworks (MOFs) as Catalysts for Air and Water Pollution Environmental Remediation. *Catalysts* **2020**, *10* (2), 195. (d) Lopez, Y. C.; Viltres, H.; Gupta, N. K.; Acevedo-Pena, P.; Levy, C.; Ghaffari, Y.; Gupta, A.; Kim, S.; Bae, J.; Kim, K. S. Transition Metal-Based Metal–Organic Frameworks for Environmental Applications: A Review. *Environ. Chem. Lett.* **2021**, *19*, 1295–1334. (e) Bhuyan, A.; Amaruzzaman, Md. Metal-organic Frameworks: A New Generation Potential Material for Aqueous Environmental Remediation. *Inorg. Chem. Commun.* **2022**, *140*, 109436. (f) Yang, C.; Xue, Z.; Wen, J. Recent Advances in MOF-Based Materials for Remediation of Heavy Metals and Organic Pollutants: Insights into Performance, Mechanisms, and Future Opportunities. *Sustainability* **2023**, *15*, 6686. (g) Wen, Y.; Zhang, P.; Sharma, V. K.; Ma, X.; Zhou, H.-C. Metal-organic Frameworks for Environmental Applications. *Cell Rep. Phys. Sci.* **2021**, *2* (2).
270. Zhu, C.; Tian, Q.; Wan, S.; Xu, H.; Hu, J.; Jing, L. Recent Progress of NH₂-MIL-125(Ti)-based Photocatalytic System in Energy Production and Environmental Purification. *Chem. Eng. J.* **2024**, *497* (1); <https://doi.org/10.1016/j.cej.2024.154689>.
271. (a) Jrad, A.; Sabeh, G. A.; Hannouche, K.; Natour, R. A.; Haidar, O.; Sammoury, H.; Ahmad, M. A.; Hmade, M. Critical Role of Defects in UiO-66 Nanocrystals for Catalysis and Water Remediation. *ACS Appl. Nano Mater.* **2023**, *6* (20), 18698–18720. (b) Liu, H.; Cheng, M.; Liu, Y.; Zhang, G.; Li, L.; Du, L.; Li, B.; Xiao, S.; Wang, G.; Yang, X. Modified UiO-66 as Photocatalysts for Boosting the Carbon-Neutral Energy Cycle and Solving Environmental Remediation Issues. *Coord. Chem. Rev.* **2022**, *458*. (c) Daliran, S.; Oveisi, A. R.; Kung, C.-W.; Sen, U.; Dhakshinamoorthy, A.; Chuang, C. H.; Khajeh, M.; Erkartal, M.; Hupp, J. T. Defect-enabling Zirconium-Based Metal–Organic Frameworks for Energy and Environmental Remediation Applications. *Chem. Soc. Rev.* **2024**, *53*, 6244–6294.
272. Razavi, L.; Raissi, H.; Hashemzahi, O.; Farzad, F. Significantly Enhanced Performance for Phenol Compounds Removal by MOF-5 Nano-Composite via its Surface Modification. *npj Clean Water* **2024**, *7*, 44. (b) Lal, S.; Singh, P.; Singhal, A.; Kumar, S.; Gahlot, A. P. C.; Gandhi, N.; Kumari, P. Advances in Metal–Organic Frameworks for Water Remediation Applications. *RSC Adv.* **2024**, *14*, 3413–3446.
273. Kandiah, M.; Nilsen, M. H.; Usseglio, S.; Jakobsen, S.; Olsbye, U.; Tilset, M.; Larabi, C.; Quadrelli, E. A.; Bonino, F.; Lillerud, K. P. Synthesis and Stability of Tagged UiO-66 Zr-MOFs. *Chem. Mater.* **2010**, *22*, 6632–6640.
274. Shen, L.; Liang, R.; Luo, M.; Jing, F.; Wu, L. Electronic Effects of Ligand Substitution on Metal-Organic Framework Photocatalysts: The Case Study of UiO-66. *Phys. Chem. Chem. Phys.* **2015**, *17*, 117–121.
275. Bazzi, L.; Boukayouht, K.; Mansouri, S.; Hankari, S. A. Eco-friendly and Cost-Effective Synthesis of Hierarchical Porous HKUST-1 from Thin Waste Electric Cables for Enhanced Cationic Dye Removal. *Proc. Safety Environ. Protect.* **2024**, *191A*, 750–759. (b) Loera-Serna, S.; Beltran, H. I.; Mendoza-Sanchez, M.; Alvarez-Zeferino, J. C.; Almanza, F.; Fernandez-Luqueno, F. Effect of HKUST-1 Metal–Organic Framework in Root and Shoot Systems, as Well as Seed Germination. *Environ. Sci. Pollut. Res.* **2024**, *31*, 13270–13283. (c) Kangra, B.; Jatana, A.; Maan, S.; Chauhan, S.; Kumar, V. Effective Adsorption of Chlorpyrifos Pesticides by HKUST-1 Metalorganic Framework. *J. Chem. Sci.* **2022**, *134*, 104.
276. Global Market Insights: URL: <https://www.gminsights.com/industry-analysis/heterogeneous-catalyst-market>. (Accessed on 20 November 2024)